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INTERNATIONAL CHEMICAL SERIES

H. P. TALBOT, PH.D., SC.D., CONSULTING EDITOR

THE  
THEORY AND APPLICATION  
OF  
COLLOIDAL BEHAVIOR

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(H. P. TALBOT, PH.D., SC.D., CONSULTING EDITOR)

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THE  
THEORY AND APPLICATION  
OF  
COLLOIDAL BEHAVIOR

Contributed by the foremost authorities in  
each division of the subject

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VOLUME II

THE APPLICATION OF COLLOIDAL BEHAVIOR

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## CHAPTER XVIII

# THE COLLOID CHEMISTRY OF MINERALS AND ORE DEPOSITS

By

WALDEMAR LINDGREN

The study of colloidal behavior from a geological viewpoint is a development of the last two decades. It was natural, indeed, that attention should first be turned to industrial and agricultural applications. The recency of such studies in geology stands out in strong relief if we examine some of the textbooks dealing with metamorphic geology published during the last 15 or 20 years. Though "katamorphism," *e.g.*, processes going on at or near the surface, is described in detail, colloid chemistry is rarely mentioned.

Van Bemmelen, besides his epoch-making studies of colloids in general and adsorption in particular, was one of the earliest (1899) contributors to the question of colloid precipitation of iron in the so-called bog iron ores.

At the present writing, in 1923, the workers have multiplied as have the problems, and the importance of the subject is more and more emphasized. The literature is very scattered, and it is most difficult for those interested in the matter to obtain even a preliminary orientation.

Two general discussions have appeared, with summaries of literature, one by R. Marc and A. Himmelbauer<sup>1</sup> in 1913, and the second by Scott<sup>2</sup> in 1922. Both are good but emphasize colloidal mineral compounds rather than colloid processes. Other briefer reviews will be found in an article by Niklas<sup>3</sup> and text-

<sup>1</sup> *Fortschritte Mineral. Krist. Petr.*, **3** (1913), 33.

<sup>2</sup> "Fourth Report on Colloid Chemistry," British Assoc. Adv. Sci., London, 1922, p. 204 (with very full lists of literature).

<sup>3</sup> *Geologie Min. Inst. Mitt. Bodenkunde*, **3** (1913), 383.

books by Boeke<sup>4</sup> and Niggli.<sup>5</sup> Liesegang<sup>6</sup> has also published a study of the subject which can be highly recommended for broad treatment and valuable suggestions.

In the following pages an attempt will be made to summarize the applications of colloid chemistry to ore deposits, and, in general, to mineral deposits. Mineral deposits are simply the result of certain phases of geological processes and, by widening the scope slightly, we shall obtain a view, perhaps rather superficial, of the rôle of the colloid state in nature. The subject is treated rather from a geological than from a strictly chemical standpoint. Many unsolved queries will be found which chemists may be able to explain. The subject is one which really should require the closest cooperation between geologists and chemists.

It is recognized that colloid processes take place by preference at the contact surfaces of air and land, or of water and land. In other words, at the bottom of rivers, lakes, and seas, in the uppermost layers of rocks, at the surface of soils, and at short distances below the surface in the zone of oxidation.

In the following we shall consider:

The minerals exhibiting colloidal behavior, and the criteria for their recognition.

Colloidal behavior at the surface and in the zone of oxidation.

Colloidal behavior in the oxidized zones of ore deposits.

Colloidal behavior in the zone of secondary sulfides in ore deposits.

Colloidal behavior in bodies of fresh water and in the sea.

Colloidal behavior in ascending warm waters.

#### THE MINERALS EXHIBITING COLLOIDAL BEHAVIOR<sup>7</sup>

Although a colloidal precipitate may initially have a composition corresponding to a certain stoichiometric formula, the tendency

<sup>4</sup> "Grundlagen der Physicalisch-Chemischen Petrographie," Berlin, 1915, p. 307.

<sup>5</sup> "Lehrbuch der Mineralogie," Berlin, 1920, pp. 434-445.

<sup>6</sup> "Geologische Diffusionen," Dresden, 1913, p. 173.

<sup>7</sup> CORNU, F.: *Kolloid-Z.*, 1-5 (1905-1910); WHERRY, E. T.: *U. S. Nat. Museum Bull. Proc.*, 51 (1916), 81; *J. Wash. Acad. Sci.*, 4 (1914), 112; ROGERS, A. F.: *J. Geol.*, 25 (1917), 530.



to adsorption may soon change this by taking up other substances in various and irregular proportions, so that the final product—a gel, for example—may be a mixture of several gels, apparently entirely homogeneous; or it may contain solutions of electrolytes; or, when hardened, it may be a mixture of gel and minute crystallized particles.

It follows from this that a hardened colloid gel does not necessarily have a definite chemical composition and, therefore, does not fulfil the common requirement of a “mineral.” Nevertheless the *approximate* composition is the same for each type of colloid “mineral” and we can hardly avoid considering it as a mineral, though it should be distinguished from the crystalloid form corresponding to it, by a separate name. “Quartz” and “opal” will exemplify this relation. Practically all colloid minerals contain or include more or less water.

Colloid minerals have a characteristic structure which, following Rogers,<sup>8</sup> we may call “colloform.” This is the structure usually designated as mammillary, reniform, botryoidal, spheroidal, oolitic, or pisolitic. This rounded or spherical form is assumed by the soft gels because they have practically the character of liquids.

Unfortunately for classification, the mineral gels do not always remain indefinitely in this condition. Temperature or time, or both, induce a crystalline structure; in other words, the development of a definite crystallized mineral from the gel. It may split so that the ultimate result will be a mixture of a crystalline mineral, or perhaps two minerals, with residuary gel of a different composition. The texture or grain of the crystalline mineral is usually a fine aggregate, most commonly a fibrous aggregate, and the fibers arrange themselves perpendicularly to the spherical or spheroidal surface of the gel. Most colloform minerals have, in fact, concentric structure and fibrous, radial texture.

The term “metacolloid,” proposed by Wherry<sup>9</sup> for microcrystalline substances of colloidal origin, is very useful and should be adopted. It is made use of in this chapter as a convenient means for designating minerals of this character.

<sup>8</sup> *J. Geol.*, **25** (1917), 518.

<sup>9</sup> *J. Wash. Acad. Sci.*, **4** (1914), 112.

The colloid minerals are often designed as "amorphous." As Rogers points out, this term is a broader one. Glass, for instance, is amorphous, but it is not necessarily in a colloid state. Long ago Breithaupt recognized this distinction when he established the two classes of "hyaline" and "porodine" (gel) minerals. In view of the discovery of the great differences in composition of normal minerals, *e.g.*, pyrrhotite, due to the presence of solid solutions, it is questionable whether the term "mineral species" can now be confined to minerals of definite chemical composition.

**Criteria of the Colloid State in Minerals.**—The colloform structure should always place a mineral under suspicion of colloid origin. This structure is not invariably present; for instance, it is not found in some varieties of hydrous aluminum silicates, nor is it always present in opal. Spheroidal structure does not necessarily indicate colloid origin; we may recall, for instance, the spherulites which form with fibrous radial arrangement during the cooling of certain silicious lavas.

If the mineral proves to be a metacolloid, then optical examination will show whether it is identical with one of the normal crystalloid minerals or a distinct species. Chalcedony is a metacolloid; it appears that some varieties of chalcedony are identical optically with quartz, while others seem to have differing optical constants.

When the material to be examined shows isotropic character in the polarizing microscope, the problem is to decide whether it is an isotropic crystalloid, a glass, or a hardened gel. The data to be determined include cleavage, specific gravity, solubility, and index of refraction.

Adsorption of dyestuffs is a characteristic on which much stress has been laid,<sup>10</sup> and it is undoubtedly true that gel minerals adsorb such materials as fuchsin, methylene blue, or malachite green much more rapidly than crystalline substances. On the other hand, it has been ascertained that finely divided materials, *e.g.*, powdered feldspar or kaolinite also adsorb considerable

<sup>10</sup> SCOTT, ALEXANDER: "Fourth Report on Colloid Chemistry," British Assoc. Adv. Sci., London, 1922, p. 211; HIMMELBAUER, A.: *Fortschritte Mineral. Krist. Petr.*, **3** (1913), 39.

amounts of dyestuffs. It seems to be a question of minute subdivision.

Another criterion is the absorption of water and the regular character of the dehydrating curves in colloids. The water, not being held in chemical combination, escapes gradually and continuously with increasing temperature. For the two groups, hydrous aluminum silicates, kaolinite (crystalloid) and halloysite (colloid), this method appears to be satisfactory.<sup>11</sup>

It should not be overlooked that there are certain crystalloids, for instance the uranium micas, which show an extraordinary power for absorbing hygroscopic water and which part with it equally easily.

The fact that a mineral occurs in an extremely finely divided state is not sufficient to warrant the conclusion that it is of colloid origin. There are, for instance, several hydrous basic ferric sulfates, like jarosite, which occur in earthy form, but which under the microscope are seen to be made up of minute but perfect hexagonal foils. Probably this is an originally crystalline precipitate.

The consideration of this case brings up the whole problem of precipitates in solutions of electrolytes.<sup>12</sup> If we produce a very slightly soluble substance it will separate in particles which, according to Von Weimarn, are always crystalline, whatever their size. Provided a disperse system is to form at all, more reaction product must be formed than can exist in true solution in the particular dispersion medium used.<sup>13</sup> We may, therefore, obtain any kind of precipitate, ranging from gels, as in the case of many sulfides, to distinct minute crystals. When these precipitates are formed in nature and dried, we may find all products from hardened gels to fine crystals, or mixtures of both.

**Development of Crystals from Gels.**—It is well known that electrolytic solutions pass freely through gels, and two such reacting solutions meeting will readily produce large crystals in the yielding gel, or Liesegang's diffusion rings may develop.

<sup>11</sup> SCOTT, ALEXANDER: *Loc. cit.*, 235.

<sup>12</sup> BANCROFT, W. D.: "Second Report on Colloid Chemistry," British Assoc. Adv. Sci., London, 1918, p. 2; BASSETT, HENRY: Fourth Rept., *Idem.* (1922), 5.

<sup>13</sup> HATSCHKE, E.: "An Introduction to the Physics and Chemistry of Colloids," London, 1922, p. 44.

Different from this is the case where crystals of the same or approximately the same composition as the gel separate not from it. Thus, natural silica gels in cavities of rocks may contain sharp and doubly terminated quartz crystals.<sup>14</sup>

Deiss prepared a gel of  $\text{MnH.AsO}_4$  by mixing equal volumes of 10 per cent  $\text{MnCl}_2$  and  $\text{KH}_2\text{AsO}_4$ . On standing 3 months, rose-colored crystals of the same composition as the gel separated out.<sup>15</sup>

**Nomenclature of Colloid Minerals.**—No uniform nomenclature as yet exists to differentiate crystalloid, colloid, and meta-colloid minerals of approximately the same chemical composition. Rogers<sup>16</sup> discusses the subject and concludes that “distinctive names are necessary, or at least advisable.” Cornu used the prefix “gel” with the crystalline modification (*e.g.*, gelvariscite) for the amorphous equivalent of variscite. Tucan<sup>17</sup> employed a similar device, except that “gel” was placed after the root name instead of before it (*e.g.*, hematogelite for colloidal ferric oxide). Wherry<sup>18</sup> proposed that the Greek letter  $\kappa$  (the abbreviation of “kolla”) be used as a prefix to the crystalline compound (*e.g.*,  $\kappa$ -limonite for stilpnosiderite). A serious objection to all these proposals lies in the fact that the amorphous mineral is not related to one polymorphous modification any more than to another. The name of any crystalline mineral connects certain crystal forms and physical properties as well as a given chemical composition. It is absurd, then, to speak of amorphous calcite or amorphous aragonite. The proper term to use is “amorphous calcium carbonate.” Still better would be “calcium carbonate gel,” but, as this in many cases might result in awkward expressions, it may be advisable to assign new mineral names, constructed on the usual plan, to such compounds. In many cases old names can be retained.

**Principal Minerals of Colloid Origin.**—In spite of the importance of colloid processes, the colloid minerals are relatively few

<sup>14</sup> HATSCHKE, E. and SIMON, A. L.: *Bull. Inst. Mining Met.*, **21** (1912), 459; LEVINGS, J. H.: *Idem.*, **21** (1912), 478; SPEZIA, G.: *Atti accad. sci. Torino*, **34** (1899), 705.

<sup>15</sup> *Kolloid-Z.*, **14** (1914), 139.

<sup>16</sup> *J. Geol.*, **25** (1917), 523.

<sup>17</sup> *Centr. Mineral. Geol.* (1913), 68.

<sup>18</sup> *J. Wash. Acad. Sci.*, **4** (1914), 517.



in number. About 1,200 well-established mineral species are known and among these only about 20 or 30 appear to be well-established colloids.

The number of gel minerals which have not been altered since their deposition is comparatively small. Much larger is the class which, though now colloform, have acquired crystalline structure, that is, the metacolloid minerals.

It is interesting to look over the 1,000 or 1,200 specimens in a textbook of mineralogy for records of metacolloids. We find a few elements, a few oxides, numerous hydroxides, a few sulfides, and quite a number of hydrous silicates. There are no sulfo-salts and few, if any, anhydrous silicates. There are many carbonates and some anhydrous sulfates. When we approach the hydrous phosphates and arsenates, colloform development is the rule rather than the exception. Reniform, mammillary, spherical forms abound and the composition is extremely variable; there are all kinds of basic and acid salts of complex formulas and often the composition is uncertain and variable. There are some hydrous sulfates, but they are less common in colloform development. Undoubtedly the prevalence of the latter groups, which mainly belong to the zone of oxidation, is due to the adsorption of phosphoric and arsenic radicals in gels.

Below is found a list of amorphous gel minerals followed by another list of metacolloids. The latter, it should be understood, are not always recrystallized gels; in most cases they may also develop as normal crystals. Siderite ( $\text{FeCO}_3$ ), for instance, sometimes appears colloform, but, as a rule, crystallizes in larger, independent individuals.

#### LIST OF AMORPHOUS GEL MINERALS

Sulfurite (S)	Allophane ( $\text{Al}_2\text{SiO}_5(\text{H}_2\text{O})_x$ )
Hydrotroilite ( $\text{FeS}(\text{H}_2\text{O})_x$ )	Cornuile ( $m\text{CuO} \cdot n\text{SiO}_2(\text{H}_2\text{O})_x$ )
Xanthochroite ( $\text{CdS}(\text{H}_2\text{O})_x$ )	Chloropal (Nontronite) ( $\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2(\text{H}_2\text{O})_x$ )
Gel-cerargyrite ( $\text{AgCl}$ )	Glauconite ( $\text{KFeSi}_2\text{O}_6(\text{H}_2\text{O})_x$ )
Opal ( $\text{SiO}_2(\text{H}_2\text{O})_x$ )	Deweylite (Gymnite) ( $4\text{MgO} \cdot 3\text{SiO}_2 \cdot (\text{H}_2\text{O})_x$ )
Hydrocuprite (?) ( $\text{Cu}_2\text{O}(\text{H}_2\text{O})_x$ )	Garnierite ( $((\text{MgNi})\text{SiO}_3(\text{H}_2\text{O})_x)$ )
Limonite ( $\text{Fe}_2\text{O}_3(\text{H}_2\text{O})_x$ )	Sepiolite (Meerschaum) ( $2\text{MgO} \cdot 3\text{SiO}_2 \cdot (\text{H}_2\text{O})_x$ )
Cliachite ( $\text{Al}_2\text{O}_3(\text{H}_2\text{O})_x$ )	
Wad (Asbolane) ( $\text{MnO}_2(\text{H}_2\text{O})_x$ )	
Halloysite ( $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9(\text{H}_2\text{O})_x$ )	

Saponite (?) ( $m\text{MgO} \cdot n\text{Al}_2\text{O}_3 \cdot p\text{SiO}_2 \cdot (\text{H}_2\text{O})_x$ )	Gel variscite ( $\text{AlPO}_4(\text{H}_2\text{O})$ )
Collophane ( $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{CO}_3 \cdot \text{F}_2) \cdot (\text{H}_2\text{O})_x$ )	Delvauxite } Hydrated ferric phosphates
Evansite ( $\text{Al}_3(\text{OH})_6 \cdot \text{PO}_4 \cdot (\text{H}_2\text{O})_x$ )	Diadochite }
	Pitticite ( $\text{FeAsO}_4 \cdot \text{Fe}_2\text{O}_3 \cdot (\text{H}_2\text{O})_x$ )
	Glockerite ( $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3 \cdot 6\text{H}_2\text{O}$ )

This list contains 25 fairly well-established gel minerals, and could probably be enlarged; there must be many more members, particularly among the phosphates and arsenates.

Next follows a list of the most prominent metacolloid minerals. A few of them are known only as metacolloids, while most of them more or less commonly show individual crystallization.

#### LIST OF METACOLLOIDS

##### ELEMENTS:

Arsenic

Gold

Platinum (?)

##### SULFIDES:

Argentite ( $\text{Ag}_2\text{S}$ )

Chalcocite ( $\text{Cu}_2\text{S}$ )

Covellite ( $\text{CuS}$ )

Metacinnabarite (?) ( $\text{HgS}$ )

Metastibnite (?) ( $\text{Sb}_2\text{S}_3$ )

Orpiment ( $\text{As}_2\text{S}_3$ )

Sphalerite ( $\text{ZnS}$ )

Wurtzite ( $\text{ZnS}$ )

Grennokitite ( $\text{CdS}$ )

Melnikowite ( $\text{FeS}$ )

Pyrite ( $\text{FeS}_2$ )

Marcasite ( $\text{FeS}_2$ )

Voltzite ( $\text{Zn}_5\text{S}_4\text{O}$ )

##### OXIDES:

Hematite ( $\text{Fe}_2\text{O}_3$ )

Cassiterite ( $\text{SnO}_2$ )

Chalcedony ( $\text{SiO}_2 \cdot (\text{H}_2\text{O})_x$ )

Goethite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )

Lepidocrocite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )

Psilomelane ( $\text{MnOH}_2\text{O}$ )

Pyrolusite ( $\text{MnO}_2$ )

Manganite ( $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ )

##### CARBONATES:

Calcite ( $\text{CaCO}_3$ )

Aragonite ( $\text{CaCO}_3$ )

Siderite ( $\text{FeCO}_3$ )

Rhodochrosite ( $\text{MnCO}_3$ )

Smithsonite ( $\text{ZnCO}_3$ )

Magnesite ( $\text{MgCO}_3$ )

Malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ )

Hydrozincite ( $\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2$ )

Hydromagnesite ( $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ )

##### HYDROUS SILICATES:

Prehnite ( $\text{H}_2\text{Ca}_2\text{Al}_2(\text{SiO}_4)_3$ )

Datolite ( $\text{H}\text{CaBSiO}$ )

Natrolite ( $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ) and other zeolites

Glauconite ( $\text{KFeSi}_2\text{O}_6 \cdot (\text{H}_2\text{O})_x$ )

Greenalite ( $\text{FeSiO}_3(\text{H}_2\text{O})_x$ )

Chamosite } (Ferrous-ferric

Thuringite } magnesium sili-

Stilpnomelane } cates, hydrous)

Chrysocolla ( $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$ )

##### PHOSPHATES:

Apatite ( $(\text{CaF})\text{Ca}_4(\text{PO}_4)_3$ )

Pyromorphite ( $(\text{PbCl})\text{Pb}_4(\text{PO}_4)_3$ )

Libethenite ( $\text{Cu}_3\text{P}_2\text{O}_8 \cdot \text{Cu}(\text{OH})_2$ )

Dufrenite ( $\text{FePO}_4 \cdot \text{Fe}(\text{OH})_3$ ?)

Collophane (a hydrous carbonophosphate, monite, quercyite)

Dahllite (a hydrous carbonophosphate)

Hopeite ( $\text{Zn}_3\text{P}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$ )

Vivianite ( $\text{Fe}_3\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ )

Strengite ( $\text{Fe}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ )

Variscite ( $\text{Al}(\text{PO}_4) \cdot 2\text{H}_2\text{O}$ )

Wavellite  $(4\text{AlPO}_4 \cdot 2\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O})$   
 Turquoise  $(\text{CuO} \cdot 3\text{Al}_2\text{O}_3 \cdot 2\text{P}_2\text{O}_5 \cdot 9\text{H}_2\text{O}?)$

## ARSENATES:

The metacolloid arsenates are mainly hydrous and basic, and are so numerous that it is scarcely feasible to enumerate them all.

Clinoclasite	} (copper arsenates)
Olivenite	
Conichalcite	
Erinite	

Symplectite (iron arsenate)  
 Erythrite (cobalt arsenate)  
 Annabergite (nickel arsenate)  
 Pharmacolite (calcium arsenate)

## SULFATES:

Barite  $(\text{BaSO}_4)$   
 Anglesite  $(\text{PbSO}_4)$   
 Alunite  $(\text{K}_2\text{Al}_6(\text{OH})_{12}(\text{SO}_4)_4)$   
 Aluminite  $(\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 9\text{H}_2\text{O})$   
 Epsomite  $(\text{MgSO}_4 \cdot 7\text{H}_2\text{O})$

There are many other sulfates which may possibly be metacolloids, but these compounds generally show a strong tendency to crystallization.

## VANADATES:

Many vanadates are in part distinctly metacolloids.  
 Vanadinite  $((\text{PbCl})\text{Pb}_4(\text{VO}_4)_3)$   
 Descloizite (Pb, Zn vanadate)  
 Volborthite (Cu, Ca, Ba vanadate)

There are thus about 70 well-known species which may have passed through a colloid stage upon their way to crystallinity. There are about 25 distinct gel minerals. These 95 species, which now are, or which have been, in form of gel, could probably be increased to 125 or 130 by including rarer minerals. Therefore, about one-tenth of the known mineral species may be ranged as of colloid origin. After all, it may happen that the gels become dried out to loose, powdery masses, in which case their original character is difficult to ascertain. Many minerals of this kind perhaps belong to the metacolloids.

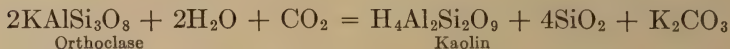
We may repeat that among them are found no amphiboles or pyroxenes, no feldspars, no spinels, no igneous or metamorphic silicates, not even when containing hydroxyl, no micas, few chlorites, and few, if any, sulfosalts.

## COLLOIDAL BEHAVIOR AT THE SURFACE AND IN THE ZONE OF OXIDATION

The surface zone in which oxidizing conditions prevail may be justly called the realm of the colloid state. In most cases the reactions proceed in solution, the water of which is of meteoric origin, precipitated on the earth as rain or snow.<sup>19</sup>

<sup>19</sup> Regarding hot springs and their deposits at the surface, see p. 463.

The meteoric waters produce weathering of the rocks, a mechanical disintegration and a chemical decomposition. Aided by vegetation and animal life, these processes result in a superficial soil in which the comminution and the decomposition reach their extreme limits. We are here chiefly concerned with the decomposition of the rocks. The minerals of the rocks, such as feldspars, mica, amphibole, or pyroxene, are not dissolved in water but decomposed by this agent. The carbon dioxide which is always contained in the water acts as a powerful aid to decomposition. Orthoclase will be decomposed into hydrous aluminum silicate, free silica, and an alkaline carbonate. An amphibole will be altered to aluminum silicate and carbonates of calcium, magnesium, and iron. This simple reaction is exemplified as follows:



According to more modern views, decomposition is the result of hydrolysis. The partly ionized water acts as a stronger acid on the weaker silicic acid and the carbonic acid combines with the bases set free. The following equation illustrates this:



Silica and kaolin would form from the latter unstable compound and the carbonic acid would form a bicarbonate with the potassium hydroxide. The silica would form a colloid sol; the aluminum silicate would likewise be in the colloid state and form sols or suspensions of varying composition or, perhaps, rather a mixture. The nature of this hydrous aluminum silicate has been the subject of much research and discussion.<sup>20</sup> The tendency seems now to be to regard it as a mixture of gels. It is known that sols of silica and aluminum hydroxides having opposite electric charges will mutually precipitate each other. We would then have the crystalline mineral kaolinite and its amorphous equivalent halloysite ( $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9(\text{H}_2\text{O})_x$ ) and, on the other hand, the amorphous mineral allophanite or allophane ( $\text{Al}_2\text{SiO}_5$ -

<sup>20</sup> Summarized by Alexander Scott in "Fourth Report on Colloid Chemistry," British Assoc. Adv. Sci., London, 1922, p. 234; and more fully in Doelter's "Mineral Chemie," Leipzig, 1917, vol. 2, Pt. 2, pp. 30-94, 120-143.



( $\text{H}_2\text{O}$ )<sub>x</sub>) (Rogers), the exact constitution of the amorphous members being more or less uncertain. Halloysite and allophane are decomposed by hydrochloric acid, while kaolinite, and perhaps some of the amorphous "kaolins," are only attacked by sulfuric acid.<sup>21</sup> That some of these gel products are mixtures can hardly be doubted.

The mode of transportation of these products is also a question which is not fully elucidated. Probably they are more generally carried by suspension in water than as true sols. In this manner they are carried out by the meteoric waters to be deposited as more or less pure clays to form sediments in rivers, lakes, and oceans. It is well known that silica is easily transported as a sol in many kinds of natural waters, but it is very rarely that such waters contain any appreciable amount of alumina. This difference in behavior leads to the suggestion that a gel mixture of alumina and silica may gradually be enriched in  $\text{Al}_2\text{O}_3$ , and that, by a leaching process, probably at higher temperatures in warm climates, bauxite or colloidal  $\text{Al}_2\text{O}_3(\text{H}_2\text{O})_x$  may result.

The alkaline carbonates are easily transported as electrolytes, but the carbonates of calcium, magnesium, iron, and manganese act differently. All of these may be carried in solution only as bicarbonates. The ferrous carbonates are easily precipitated, and, by electrolysis, ferrous hydroxide is formed which also easily oxidizes to ferric hydroxide gel, which may be transported. When pyrite is present, ferrous and ferric sulfates are formed, from which again ferric hydroxide may be developed.

It is easy to obtain true ferric hydroxide sols from almost all ferric salts, and it is possible that transportation of such sols can be a factor of much importance. "Protective colloids" serve to delay coagulation. One such "protector" is furnished by the organic "humic" compounds in the sol. No doubt this is an important process, particularly in the deposition of bog

<sup>21</sup> J. W. Mellor argues with some justification that this amorphous kaolin, insoluble in hydrochloric acid, is the colloid equivalent of kaolinite, and has given it the rather unfortunate name "clayite." The studies of clays may frequently be criticized by absence of exact microscopic examination, previously to undertaking determination of dehydration curves, etc. See SOMERS, R. E.: "Microscopic Study of Clays," U. S. Geol. Survey *Bull.* 708 (1922), 292-305.

iron ores and bog manganese ores. As the solutions descend below the surface such "protective" agents probably lose their power.

Manganese carbonate is equally easily precipitated from a solution of bicarbonate, and hydrolyzed to manganese hydroxide, which again is oxidized to  $\text{MnO}_2$ . Extensive transportation of  $\text{MnO}_2$  undoubtedly takes place in nature and manganese sols may easily be formed; here, too, the protective action of humus substances may be important. It is probable that silica sols may also act to some degree as protective agents.

Another process of great importance is the adsorption of substances by the coagulated gels. The adsorption of phosphoric acid and potash is well known as an essential part of soil formation. Gels of ferric hydroxide, manganese dioxide, and aluminosilicates have the power to adsorb many bases and radicals, such as phosphoric acid, arsenious acid, vanadic acid, and the oxides of barium, lithium, potassium, cobalt, nickel, copper, etc. According to the researches of E. Kohler<sup>22</sup> and E. C. Sullivan,<sup>23</sup> colloidal minerals like kaolin and many other finely divided substances adsorb, for instance, copper from a percolating solution of copper sulfate. Here, it appears, there is a chemical process, an exchange of bases. In this case alumina is given up by the kaolin, and copper substituted. Probably not all processes of adsorption are of this kind. Cornu<sup>24</sup> believes that any base, for example ferric hydroxide gel, may adsorb, say, phosphoric acid until a certain amount approximately corresponding to a chemical compound is formed which may crystallize later out of the gel.

It remains to mention another phenomenon of importance, that is, the concentric rings in rhythmic repetition of certain substances, for instance, iron oxide, which form during colloidal processes in weathering, and are best illustrated by the banded agates,<sup>25</sup> and various concretionary deposits. In general, they are formed as shown by experiments where an electrolyte penetrates a gel. If a reaction involving a precipitate takes place in a

<sup>22</sup> *Z. prakt. Geol.*, **11** (1903), 49.

<sup>23</sup> *U. S. Geol. Survey Bull.* 312 (1907).

<sup>24</sup> *Kolloid-Z.*, **4** (1909), 15, 89.

<sup>25</sup> LIESEGANG, R. E.: "Geologische Diffusionen," Dresden, 1913.

gel, then the precipitation does not take place uniformly but in rhythmic succession, forming rings or layers. Evidently it has to do with recurrent periods of supersaturation.<sup>26</sup>

The decomposed and disintegrated rock of the upper zone of oxidation is, in general, a mass of residual minerals mixed with aluminosilicate gels, silica gel, and iron, manganese, etc., in various forms. The tendency is towards the development of concretionary structures, localized in various places either in the mass or at the bottom where the disintegrated rock borders against unaltered rock. Thus, limonite with adsorbed phosphoric acid forms to considerable deposits, or manganese dioxide—wad and psilomelane—develops in concretions. In warm climates ferric oxide and bauxite (a mixture of gels of aluminum hydroxide and partly crystallized products) develop into masses of economic importance. The occurrences suggest that, besides deposition in open cavities, there are processes of replacement going on with exchange of constituents between the residual mass and the solutions.

Near the bottom of the decomposed zone we find colloform masses of barite, of phosphates, like collophane and variscite, of zinc carbonate (smithsonite), and many other substances.

#### COLLOIDAL BEHAVIOR IN THE OXIDIZED ZONES OF ORE DEPOSITS

The discussion of conditions in the oxidized zone of rocks naturally applies also to ore deposits, for they are only specialized rocks. The reactions, however, are here much more complicated, involve a greater number of elements and minerals, and, in sulfide deposits, the presence of sulfuric acid gives a distinct facies to the phenomena.

In ore deposits, as elsewhere, the water level may be considered as the lower limit of the zone. It is not necessarily the present water level which counts, but the one obtaining when the main part of the oxidation took place. This depth may be less than 50 ft. and, exceptionally, it may be 2,000 ft. or even more.

The action of atmospheric waters, aided by sulfuric acid, tends to destroy original texture of the ore, and opens spaces, resulting in vuggy or honeycombed structure alternating with

<sup>26</sup> BRADFORD, S. C.: *Biochem. J.*, **14** (1920), 474.

clayey masses. Concretionary and stalactitic forms are common, also nodular masses in which the oxysalts of the metals are present in successive shells. Reticulated fractures are filled with secondary products. While oxysalts predominate, some secondary sulfides may form where oxygen locally was deficient. The ultimate products here, too, are limonite, kaolin, wad, or psilomelane, and residual quartz, gold, cassiterite, or any other insoluble mineral. All the soluble products, copper minerals, for instance, tend to migrate downward. The various metals tend to segregate in separate masses of oxysalts; thus, intergrown galena and sphalerite separate into masses of cerussite and smithsonite. Some parts of the ore deposits become enriched; others impoverished.

Regarding the part which colloid processes play in this infinite complexity of reactions, there is still much to learn. In general, the solutions are acid, contain little silica, and, so far as known, no protective colloids. Most of the gel products must be derived from hydrolysis or electrolytic reactions. Probably few sols can maintain themselves long in this mixture of strong electrolytes.

Among the colloform products there are limonite, psilomelane, sometimes hematite. Coatings of chalcedony occur sometimes, especially in deposits poor in pyrite. The reactions proceed as outlined above except that the starting point is usually ferrous sulfate instead of ferrous carbonate. Colloform phosphates, arsenates, and carbonates (malachite, smithsonite) are common. Sericite or white mica is usually present in the primary deposits. Under the influence of sulfuric acid solutions this sericite changes to kaolin or similar minerals. Continued strong action of the same reagent ultimately develops residual quartz and sometimes colloform alunite.

Gold and silver are set free from sulfides or tellurides, in which they are in fine distribution, and may be transported for some distance as sols. Bastin,<sup>27</sup> for instance, has shown how a gold sol may develop by the action of sulfides on gold chloride solutions. The same may happen to silver, and it is almost certain that precipitated silver chloride may be carried a long distance in colloidal suspension.

<sup>27</sup> *J. Wash. Acad. Sci.* (Feb. 4, 1915), 64.



COLLOIDAL BEHAVIOR IN THE ZONE OF SECONDARY SULFIDES  
IN ORE DEPOSITS

It is evident that downward percolating waters have dissolved a large amount of salts from the oxidized zone of ore deposits and the migration of these solutions continues, though at a much slower rate, below the water level. These solutions carry sulfuric acid, gradually being neutralized on the downward course, and a large amount of sulfates of iron, copper, zinc and other rarer metals. They now contain only a small amount of colloidal material, in most cases only a little silica. The acid or neutral solutions may, however, react with unaltered sulfides in the primary ore. Pyrite, bornite, chalcopyrite, for instance, react with the descending cupric sulfate and, while iron goes into solution, cupric or cuprous sulfide is precipitated, that is, covellite or chalcocite. By similar reactions sulfides of silver or native silver may form, occasionally other sulfides like sphalerite or galena. The new sulfides are richer and in this manner an enriched zone of, say, chalcocite or covellite may form below the oxidized zone. In part, this process is a direct replacement by which solid crystalline chalcocite replaces pyrite, for instance, with preservation of volume. Part of the new sulfides are, however, soft and "sooty" or powdery, and evidently have been formed as a colloid precipitate in the descending solution; in places the precipitate has hardened to a mammillary mass which now shows extremely fine-grained texture, that is, it is a meta-colloid.<sup>28</sup> Generally, it is close to or deposited upon pyrite. Covellite, also secondary argentite or silver sulfide, frequently shows the same physical conditions. The secondary sulfides are, therefore, in part, crystalline replacements of sulfides and in part colloidal precipitates. It is known that sulfuric acid attacks pyrrhotite, galena, and sphalerite, to much less extent pyrite,<sup>29</sup> and the hydrogen sulfide set free would precipitate colloidal sulfide from metal solutions. To a degree, the powdery sulfides owe their origin to such a reaction.

<sup>28</sup> TOLMAN, C. F., JR.: *Trans. Am. Inst. Mining Met. Eng.*, **54** (1917), 411.

<sup>29</sup> TOLMAN, C. F., JR. and CLARK, JOHN D.: *Econ. Geol.*, **9** (1914), 559.



## COLLOIDAL BEHAVIOR IN BODIES OF FRESH WATER AND IN THE SEA

The mineral deposits formed in fresh waters include those of limonite (bog iron ore) and soft black manganese ore (mainly wad or hydrated  $\text{MnO}_2$ ). Neither of them is of great importance. The ores form colloidal precipitates which, in part, may harden to metacolloids.

The rivers and lakes are the first recipients into which the percolating waters are discharged. Organic matter is nearly always present and biological processes play an active rôle. In part, the iron doubtless is held in solution as carbonate or sulfate, in part, as hydroxide sols protected by humus colloids. The precipitation is partly by flocculation, partly also by bacterial reactions,<sup>30</sup> in which the end products are colloid precipitates. Adsorption plays an important rôle and we generally find that the ores contain phosphorus, arsenic, and vanadium. In peat bogs or swamps, where there is an abundance of organic matter and sulfur, siderite or even slimy iron sulfides may be formed. In beds formed in brackish water the siderite may form rounded concretionary masses, doubtless first deposited in the colloid state. These are the so-called sphaerosiderites. These concretions, often found in sedimentary beds, in many cases owe their origin to later migration and colloid precipitation after the beds have been deposited but before the strata have hardened.

In the stagnant waters of the Black Sea, micro-organisms liberate hydrogen sulfide, which by reaction with the iron in the sediment produces black iron sulfide; this again may slowly crystallize to pyrite or marcasite.

Another instance of biochemical colloidal reactions are the diatomaceous beds made up of opaline silica, secreted in the shells of these organisms.

The sea forms the ultimate receptacle for the salt solutions derived from the decomposing rock. At first glance it would seem that this medium would be unfavorable for colloid reactions, but here, even more than elsewhere, biochemical processes

<sup>30</sup> HARDER, E. C.: U. S. Geol. Survey, *Prof. Pap.* 113 (1919).

dominate and the organic colloidal material plays an important protective rôle.

Just as concretionary and pisolitic structures are characteristic for the colloidal ore deposits on land and in fresh water, so the oolitic structure is apt to be characteristic for the deposition in the sea, though here, too, larger concretionary forms may occur. In many, if not in all, cases, micro-organisms aid in the development of the minute spherical oolites.

**Clays.**—The coarser suspensions, as well as the sols (like silica) and mixed flocculated material of aluminum hydroxide and silica, are rapidly precipitated in sea water and form beds of material grading into pure clays, pure enough to be of economic importance. Naturally, the fineness of the precipitate stands in some relation to the distance from the land. Even deposits of bauxite (mixed aluminous hydroxides) are claimed to result from marine deposition. Possibly, however, this bauxite may be transported.

**Limestone.**—The calcium carbonate in solution contributed by the rivers may be precipitated by a simple reaction as soon as the streams reach the sea. Limestone may also be formed by sedimentation of suspended particles. But the most important mode of formation is undoubtedly by biochemical reactions. The carbonate of calcium may be taken up by organisms directly from the surface layer of sea water, which is saturated with respect to this salt, or ammonium carbonate may be formed bacterially from nitrates or albuminous matter, which again reacts with the calcium sulfate in the sea water to form calcium carbonate. The calcareous oolites which are so common are believed to be formed by bacteria by some such process.

Molluscs and other inhabitants of the sea also precipitate calcium carbonate to form their shells, in part, as aragonite, gradually changing to the more stable forms of calcite.

But in all cases probably the deposition begins by the precipitation of minute particles which, whether we regard them as ultra-microscopic crystals or not, really form a colloidal precipitate arranging itself often in spherical form and rapidly recrystallizing to fibrous aragonite.<sup>31</sup> Likewise, all shells, corals, etc.,

<sup>31</sup> JOHNSTON, J. and WILLIAMSON, E. D.: *Am. J. Sci.* (4), **41** (1916), 473.

appear to grow after the same manner, that is, beginning by a colloid precipitate.

**Deposition of Iron Minerals.**—The most common of the marine iron silicates is glauconite<sup>32</sup> (see page 452) which forms abundantly in marine sediments of many places and ages, though it scarcely ever occurs in such quantities as to form iron deposits. Glauconite occurs as small green concretions, but is not oolitic. It is certainly a colloid mineral and Hummel regards it as a product of absorption of potassium and silica in a ferric hydroxide gel. Generally, it occurs with remains of organic life. Hummel likewise holds that it is formed in cold waters rich in oxygen in contrast to the iron oolites which are believed to be a product of warm seas. Thus is again emphasized the dependence of the geological colloid processes on climatic conditions.

The principal marine iron ores are oolites of hematite, chamosite, thuringite or greenalite, and siderite, all of which are most likely formed by biochemical processes. There is probably no oolitic limonite of marine origin, though subsequent oxidation when exposed to the air may develop it. The minute concentric and often fibrous shells of each oolitic grain may consist of all or any of the three minerals mentioned. It is characteristic that the iron silicates enumerated above are always ferro-ferric silicates. They are held to accumulate in warm seas and near the shore, probably deriving their iron from the waters draining the adjacent continents.<sup>33</sup> In all cases the iron oolites doubtless represent gels precipitated or condensed by complex biochemical reactions close to the shore. The iron oolites always contain adsorbed phosphorus.

Another important class of deposit is formed by the marine phosphates. Generally, they are carbonophosphates like collophane or dahllite, and they are widely disseminated in sedimentary series. Unquestionably, they are of organic origin, for all organisms contain phosphorus. When concentrated to important deposits, they appear characteristically in concretionary or oolitic form, evidently hardened and, in part, crystallized gels. The exact mode of origin is in doubt; it is believed that

<sup>32</sup> CLARKE, F. W.: "Geochemistry," U. S. Geol. Survey *Bull.* 695 (1920), 511; HUMMEL, K.: *Geol. Rundschau*, **13** (1922), 40–136 (with literature).

<sup>33</sup> HAYES, A. O.: Can. Geol. Survey, *Mem.* 78 (1915).

ammonium phosphate may form in organic matter and that this reacts on shell remains forming calcium phosphate.

Other marine deposits which may appear in oolitic form are pyrite (or marcasite), psilomelane, and barite.

It is evident that the mineral deposits formed in the sea are largely of colloid origin.

### COLLOIDAL BEHAVIOR IN ASCENDING WARM WATERS

In large part, the atmospheric waters descending in the rocks ascend again on fissures and now have a higher temperature and an increased salinity. There are also, particularly in volcanic regions, ascending hot springs, heavily charged with salts. Part of this water may be of atmospheric origin, but some of it is surely of more deep-seated origin and derived from the magma. Also, it may in part be derived from the dehydrating of rocks under metamorphic processes.

Some of these waters contain as much as 700 parts per million of silica and chemists agree that it is carried in colloidal solution. At the orifices of such springs, opal and, more rarely, chalcedony and quartz are deposited, forming so-called silicious sinters. The dissolved carbonates are sometimes colloform, as so-called pisolitic structures—a sort of coarse oolite. Other substances in the water may also be precipitated in colloidal form, for instance, limonite or psilomelane with adsorbed substances, and sulfides such as<sup>34</sup> those of iron and antimony. The colloform psilomelane may contain many adsorbed substances, such as barium, copper, and tungsten.

Below the surface most of the minerals separate as crystalloids. The silica, however, frequently takes the form of chalcedony, the concentric crusts of which give evidence of colloid origin, or of fine-grained fibrous aggregates, as chert, jasper, or jasperoid, or, finally, of granular quartz in which, crossing the grains, still may be seen the concentric, mammillary outlines of deposited gel.<sup>35</sup> This is mainly observed in deposits

<sup>34</sup> At Steamboat Springs, Nevada, enough red antimony sulfide is deposited to impart a red color to the sinter. See BECKER, G. F.: U. S. Geol. Survey Mon. 13 (1888).

<sup>35</sup> LINDGREN, W.: *Econ. Geol.*, **10** (1915), 225.



which have been formed at a short distance below the surface, as at Waihi, New Zealand, and Tintic, Utah, but there are also many cases in which there is no definite evidence of colloidal origin in the structure of the quartz.

We may assume that quartz has generally crystallized from a silica gel or a silica sol up to the temperature limit at which such a colloid may be stable. Königsberger<sup>36</sup> in his experiments has obtained chalcedony at 350°C., which may for the present be regarded as the upper limit. Most ore deposits have probably been formed below this temperature, but the fact remains that chalcedony is confined to the deposits which originated near the surface. Another interesting feature, first mentioned by J. D. Irving and later described by W. Lindgren,<sup>37</sup> is the replacement of limestone by a silica gel recrystallizing to a cryptocrystalline aggregate which may preserve the structures of the original rock. By reaction between electrolytes in this gel a banded structure of small grains of galena and sphalerite resulted, somewhat similar to Liesegang's rings.

A. N. Winchell,<sup>38</sup> and later W. Lindgren,<sup>39</sup> held that the quartz veins at National, Nevada, had been formed from a gel containing gold. Carnaval<sup>40</sup> in 1910 expressed the view that certain pyritic deposits had formed by crystallization from silica gels, charged with metallic sulfide. Hatschek and Simon hold the same view in regard to gold quartz veins.<sup>41</sup>

This brings up the question of colloidal gold disseminated as a sol in silica gels. While the more deep-seated veins generally carry fairly coarse free gold, those found near the surface are often distinguished by an extremely fine distribution of the metal, so that it is impossible to show it by any other process but analysis, assaying, or cyaniding. Hatschek succeeded in dispersing gold in gels and caused it to be deposited later in metallic particles by using reducing substances, such as oxalic acid and ferrous sulfate. He also produced banding in a some-

<sup>36</sup> *Centr. Mineral. Geol.*, Nos. 11 and 12 (1906).

<sup>37</sup> *Econ. Geol.*, **6** (1911), 527; **10** (1915), 225.

<sup>38</sup> *Mining Sci. Press*, **105** (1912), 655.

<sup>39</sup> *U. S. Geol. Survey Bull.* 601 (1915), 48.

<sup>40</sup> *Z. prakt. Geol.*, **18** (1910), 181.

<sup>41</sup> *Bull. Inst. Mining Met.*, **21** (1912), 450.



what similar way as Liesegang's rings. Holmes<sup>42</sup> has further elaborated the technique of the crystallization of various substances in silica gel. Later, Dreaper<sup>43</sup> showed that such imitation of banding could be produced in finely powdered substances as well as in gels, and, in fact, in capillary tubes. Still later, Bastin showed (see page 458) that gold can very easily be dispersed by the action of some sulfides in a gold solution. Undoubtedly these experiments have great significance, though the results probably should not be extended to cover all kinds of gold deposits.

In a series of experiments Tolman and Clark<sup>44</sup> showed how copper sulfides could be dispersed by hydrogen sulfide in alkaline and even in acid solutions and again precipitated. The precipitation occurred upon the escape of the hydrogen sulfide. These experiments are highly significant, even if the full scope of their application is as yet not clear. They probably illustrate well certain phases in deposition taking place in ascending hot waters.

The study of ore deposits has, in many places, shown a marked difference in composition of filled fissures in comparison with the adjoining, partly altered rock. This suggests an osmotic action of the porous wall rock, which has dialyzed the ascending solutions, allowing electrolytes and gases to pass while colloidal silica and certain associated substances, like gold, would be retained in the fissure.<sup>45</sup> Undoubtedly, such osmotic action has taken place and the process deserves more detailed study.

The preceding pages simply aim to give a summary, in briefest outlines, of the application of colloid chemistry to mineralogy and geology. The impression is that of a broad field imperfectly cultivated but promising rich returns to the tillers who are willing to expend work and brains in raising adequate crops.

<sup>42</sup> *J. Franklin Inst.* (1917), 743.

<sup>43</sup> *Bull. Inst. Mining Met.*, **23** (1914), 381.

<sup>44</sup> *Econ. Geol.*, **9** (1914), 559.

<sup>45</sup> BECKER, G. F.: U. S. Geol. Survey, Eighteenth Am. Rept. *Mineral Resources*, pt. 3, (1892), p. 157; LINDGREN, W.: *Trans. Am. Inst. Mining Met. Eng.*, **30** (1900), 691, and elsewhere.

## CHAPTER XIX

### THE COLLOID CHEMISTRY OF THE SOIL

By

MILTON WHITNEY

The colloidal material of the soil is assuming a position of great importance in the study of the soil as a whole, as it is evident that this material is the seat of most important dynamic forces which give the soil type much of its characteristic relations to agriculture. Studies upon the chemical and biochemical reactions of the soil colloids<sup>1</sup> are clearing up conditions which the mineral chemistry, as relied upon until recently, could not explain.

#### ORIGIN OF THE SOIL COLLOIDS

The soil colloids are derived from two principal sources. The remains of plant and animal life, together with the living and dead soil organisms, all of which are largely colloidal in nature, give rise to the organic colloidal material of the soil. In most agricultural soils these organic colloids form a small proportion of the total colloidal matter present, but in cases of arrested biochemical activities, particularly under saturated conditions, we have a class of organic soils, such as the peats and mucks, in which the colloids are mainly organic in nature. The greater portion of the colloids in most agricultural soils is of mineral origin. It is derived principally from the breaking down of complex silicates.

In the mechanical analysis of soils, where the materials are separated according to size even down to the clay group, the

<sup>1</sup> The term "soil colloid" as used in this chapter is synonymous with "colloidal material of the soil," and is used for convenience and brevity. The conception of a colloid as a *state* or *condition* of matter is maintained.

upper limit of which is 5 microns, the unaltered minerals have a characteristic angular form which indicates a small solvent action of the water surrounding them. When we enter the clay group, however, and study the material below 5 microns in diameter, we find very few particles of unaltered mineral material, while about 90 per cent of the particles constituting the clay group are colloidal aggregates somewhat indurated.

In shaking a soil with water preliminary to the mechanical analysis, the soil falls apart into the individual unaltered mineral grains, covered probably by a very thin coat of colloidal material, and into colloidal masses more or less indurated, the greater proportion of which fall into the clay group, a smaller proportion into the silt group, while a few are large enough to separate out with the several sand grades.

The low-power centrifuge used in the mechanical analysis, having a force of about 150 gravity, permits of the separation of the silt and clay groups under microscopic control. When, however, the turbid liquid containing the clay particles, which remain suspended under a force of 150 gravity for a sufficient time for the separation, is introduced into a supercentrifuge with a force of 17,500 gravity, not over 1 or 2 per cent of the soil comes through as colloidal material, the rest being thrown out with the unaltered minerals. To obtain a further separation of the true colloidal material through the supercentrifuge requires further agitation of the soil in water when an additional amount of colloid will be yielded. So difficult is it to get the soil colloid into this highly dispersed form that even after 50 washings one can expect to obtain only from 30 to 50 per cent of the colloidal material in the soil.

The most recent investigations indicate that there is not over 2 to 3 per cent of unaltered mineral material of the soil that is below 5 microns in diameter and that there is practically no unaltered mineral material in the soil below 0.1 micron in diameter. It appears, therefore, that the finer minerals disappear comparatively rapidly in the soil and a large part of the material contained in them appears in the colloidal state. This view seems quite reasonable, for the finer the material the greater are the contact surfaces per gram and, consequently, the more rapid is the decomposition.

## CHEMICAL NATURE OF THE SOIL COLLOIDS

Conceptions regarding the chemical composition of soil colloids in the past have been based largely on inference. During the early days of soil investigation, it was naturally assumed that the finest particles in the soil, those of colloidal dimensions, were of the same nature as the larger particles, differing only in size. This view, however, did not satisfactorily explain the reactivity of the soil with inorganic salts. Later, it was, therefore, assumed that the finest particles of the soil consisted chiefly of especially reactive minerals, the zeolites. This view also was discarded later when it became evident from mineralogical investigation that definite crystalline zeolites could rarely, if ever, be identified in the soil. The existence of zeolite-like compounds was then postulated. It is now coming to be quite generally believed that the inorganic colloidal material of the soil is essentially the same as the artificial gels of silica, iron, and alumina, which have been prepared.

It is noteworthy that these different conceptions have been based chiefly upon the behavior of the soil as a whole. Very little work has been done on the chemical composition of the pronouncedly colloidal material actually isolated from the rest of the soil, although analyses have been made of the finest soil separates, which probably consist chiefly of colloidal material.

The separation of large amounts of colloidal material from the soil by a supercentrifuge imparting a force of 17,500 gravity has made it possible to investigate this material more thoroughly than ever before. In the dilute solutions, sometimes showing only an opalescence and rarely carrying over 4 g. of colloidal material per liter, the particles are so small that under the ultramicroscope they appear like droplets, just as fat globules in milk, though generally smaller. When this material is collected on the outside of a Pasteur-Chamberland filter through suction, it concentrates into a jelly-like material. When dried, it is a hard, horn-like mass and in a thin coating on glass it usually has an amber-yellow color and is brittle like a resin. A very thin film sticks to glass, porcelain, or platinum with great tenacity and is removed with great difficulty. No evidence can be seen in any microscopical examination of any structure or form.



The fundamental reason for the formation of colloidal matter in soils is that 97 per cent of soil material is of igneous origin and is not stable in water. Under the solvent action of water the complex silicate minerals yield insoluble hydrolytic products of iron, aluminum, and silicon and soluble hydrolytic decomposition products of calcium, magnesium, sodium, and potassium. In this way, products of two different natures are formed, one the soil colloids, and the other the truly soluble material of terrestrial waters. If our concept is correct, that the colloidal material is derived principally from the breaking down of the finest of the soil minerals through the action of water, with the formation of complex hydrates of silicon, iron, and aluminum, it seems probable that at the moment when the change of state occurs we have no definite compounds, but mixtures of colloidal silicic acid, aluminum hydroxide, and iron hydroxide adsorbing a part of the electrolytes that had first gone into true solution.

From this point onward, however, aging effects occur and we may have the formation of complex silicates. The material is subjected to wetting and drying with the fluctuations of the rainfall. It is subjected to changes of pressure, and to fluctuations of the atmospheric gases, particularly carbon dioxide. They are in the stream of a circulatory system which is continually flowing first in one way and then in another. In the course of time, and according to conditions, there may be a separation of the silica, of the alumina, or of the iron, and there may be a segregation such as would account for the formation of secondary quartz, of iron ores, of kaolinite, of bauxite, of laterite, and of the ordinary hardpan which forms below the surface of the soil. These are secondary effects which must be considered to explain the occurrence of mineral deposits and must be considered in connection with the chemical composition of colloids collected at any particular place, because the sample of soil from which we extract the colloid has been subjected more or less to this aging process, and may have contained at the time it was collected the original colloids formed in the sample itself, or it may have lost or gained colloidal material to or from adjacent layers or to or from more distant layers of soil.

Recent analyses have been made by the Bureau of Soils of the colloidal material obtained from 44 selected soils, representing



the important soils of the United States. The colloids obtained from the soil and subsoil were remarkably uniform in composition. Those obtained from very different soil types were fairly uniform with respect to silica, alumina, iron, and combined water, the mean deviation being only from 10 to 15 per cent of the average of each of these substances. The variation in the other constituents was much greater, as will be seen from the following table:

TABLE I

Constituent	Average, per cent	Mean deviation from average, per cent	Mean deviation as part of average, per cent
SiO <sub>2</sub> .....	43.130	4.640	10.7
Al <sub>2</sub> O <sub>3</sub> .....	27.070	4.090	15.1
Fe <sub>2</sub> O <sub>3</sub> .....	10.400	1.530	14.7
TiO <sub>2</sub> .....	0.640	0.150	23.4
MnO .....	0.110	0.070	63.6
CaO .....	1.020	0.580	56.8
MgO.....	1.630	0.750	46.0
K <sub>2</sub> O.....	1.420	0.750	52.1
Na <sub>2</sub> O.....	0.370	0.190	51.3
P <sub>2</sub> O <sub>5</sub> .....	0.280	0.120	42.9
SO <sub>3</sub> .....	0.110	0.060	55.0
Cl.....	0.033	0.007	21.0
Combined H <sub>2</sub> O.....	10.400	1.630	15.6
Organic matter.....	3.400	1.670	49.1
N.....	0.260	0.110	42.1

It will be noticed at once that the composition of these colloids is very unlike the composition of the soil minerals. The silica is much lower, while the alumina and iron are higher. The contrast between the chemical composition of soil minerals and the soil colloidal material is shown in Table II.

The total depth of the soil and subsoil from which these colloids were extracted was not over 36 in. In the process of aging has the silica moved down below this depth, or has it gone into the formation of secondary quartz? Have the alumina and iron

shown a tendency to accumulate in the soil and subsoil colloids? These are questions that can only be answered by extending the investigations into greater depths below the surface and, perhaps, from the study of secondary minerals and secondary rocks.

TABLE II

Soil material	Percentages of							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	Com- bined H <sub>2</sub> O
Wabash soil non-colloidal mineral material.....	82.84	8.79	0.60	0.59	0.43	2.66	1.63	0.64
Wabash soil colloidal material...	51.28	20.28	9.75	2.19	2.09	1.91	2.10	7.10
Orangeburg soil non-colloidal mineral material.	97.02	0.69	0.32	0.14	0.02	0.43	0.13	0.79
Orangeburg soil colloidal material. .	40.35	31.04	10.11	0.51	0.73	0.81	0.24	11.10

The percentages of the more soluble bases appear higher in the soil and subsoil colloids than in the minerals from which they are likely to have been derived. Is there evidence here of a surface accumulation of these materials in the colloids near the surface of the earth coming up from lower levels?

We have, on the one hand, visible evidence of the segregation and accumulation at or near the surface of the earth of vast accumulations of ore deposits which have evidently come up from great depths in very dilute solutions in the circulatory waters of the earth and have come to rest at certain locations favorable to their precipitation in solid masses. Have we here also evidence of accumulation of the more soluble elements, such as calcium, potassium, phosphorus, etc., at the surface to maintain the surface soil against loss from erosion and human occupation?

## DETERMINATION OF THE COLLOIDAL MATERIAL OF SOILS

Three principal methods have been used in the recent work of the Bureau of Soils for the estimation of the amount of colloids in soils: (1) the adsorption of water vapor, (2) the adsorption of ammonia gas, and (3) the adsorption of malachite green in both the soil and its colloid, and determining the ratio of one to the other.

The method of the adsorption of water vapor is conducted briefly as follows: The soil is first leached of any excess of soluble salts it may contain and is then brought to an air-dry condition. The colloid previously separated from larger samples of the soil is air-dried and crushed to a fine powder. Usually 2 g. of soil on the air-dried basis and the same amount of the colloid are exposed in thin layers in wide-mouthed weighing bottles and put into desiccators containing 2 per cent sulfuric acid (by volume). The desiccator is then evacuated to 50 mm. or less, which is nearly the vapor pressure of water at a temperature of 30° C. The desiccator is put in a constant temperature air bath regulated at 30° C. and left for 5 days. The bottles are then immediately stoppered and weighed. They are then dried at 110° C. for 18 hours and the weight again taken. The ratio of the adsorption of the colloid to the adsorption of the soil gives the percentage of colloid in the soil. The average adsorption of soil colloids is about 30 per cent of water, the adsorption of water vapor by the soil, of course, being dependent upon the amount of colloid present. The range of adsorption of soil colloids, so far as determined, is from about 24 to about 35 per cent, but it has been found that the mean of 30 per cent can be used in calculating the amount of colloid present in the soil with comparatively slight error. Most of the samples which have been examined come within 2 or 3 per cent of this average.

In the adsorption of ammonia, usually from 3 to 5 g. of the soil, or an equal amount of the soil colloid, are put into a U-tube, which is immersed in boiling water and evacuated to a very low pressure with a Mays-Nelson vacuum pump, after which the U-tube is removed from the boiling water, surrounded with crushed ice to secure a temperature of approximately 0° C., when ammonia gas is passed over the soil until saturation is

attained, after which the U-tube is again placed in boiling water and is again evacuated, the ammonia given off being collected in boric acid solution and titrated.

In the adsorption of malachite green, a gram or less of soil or colloid, depending upon their capacity to adsorb, is shaken in water in rotating tubes for 18 hours, then sufficient sodium oxalate is added to the soil to throw down any free lime that may be present, a certain volume of standard malachite green solution is added, and the tubes are again rotated for a short time. Then the solutions are centrifuged in small tubes and the supernatant liquids are withdrawn and the amount of dye estimated colorimetrically. In this method the adsorptive capacity of the material taken must be considered, as it is important to have the end concentration of the dye reasonably close to that of the standard for accurate readings.

These three methods usually give quite concordant results. Where they differ, the results from the ammonia adsorption are apt to be higher than by the water method and the results from the dye adsorption lower. When certain corrections for the extractable and unextractable colloidal material are applied in the ammonia and dye methods, these methods yield very concordant results. Without corrections, the water-vapor method yields results which are believed to be very near the truth, although under these conditions the method is not quite as exact as the ammonia or the dye methods when the corrections are applied.

The results of these methods have been checked up in various ways through persistent attempts, by many washings, to separate all of the colloid possible by this method, with a determination of the colloids left in the different separates of larger diameters. They have also been checked up by actual microscopic counts of colloidal aggregates left in the soil separates. They have also been checked up with the crushing strength of briquets, so that the accuracy of the methods has been substantially confirmed by different and independent methods.

The difficulty in securing a separation of the colloidal material in a dispersed state from the indurated condition in which it occurs in soil has lead to the belief, generally stated in the literature, that there is not over 1 or 2 per cent of colloid in the soil.



In the 44 samples which have been studied by the Bureau of Soils, it appears that the colloidal content varies from around 6 per cent for the sandy soils to upward of 60 per cent for some of the most plastic clays of the Houston and the Sharkey series. The ordinary loam soils, upon which our general farming is carried on, range from 15 to 25 per cent of colloid material. On the other hand, samples of deep sea deposits collected at depths from 1 to 3 miles show 100 per cent colloid when the shells are excluded. Many local deposits of material also show from 70 to 80 per cent when collected from land surfaces. This, in brief, is the fragmentary information as to the content of colloids in soils at the present time.

#### BEHAVIOR OF THE COLLOID MATERIAL OF SOILS

The remarkable adsorptive properties of soils and of soil colloids for water, gases, vapors, mineral elements, and certain organic bodies show a marked and rather regular decline as the material is heated above  $110^{\circ}\text{C}$ . At half of the property is lost at  $500^{\circ}\text{C}$ . and practically all of it has gone when the material has been heated to  $900^{\circ}$ , although there is no evidence of even incipient fusion at this higher temperature. Finely powdered colloid exposed to this higher temperature, when cooled down, is still pulverulent, shows no rounding of the edges under the microscope, but it adsorbs practically no moisture and does not swell up when shaken with an excess of water. Below  $110^{\circ}\text{C}$ . it can be subjected to changes of temperature without apparent effect on its adsorptive powers under uniform temperature and moisture conditions.

It is the colloid that gives plasticity to the soil when wet and hardness to the soil when dry. No satisfactory methods have been devised for measuring plasticity in a mass of material, such as the soil is composed of, but the strength of the colloid when the soil is dried may be fairly measured by the strength of briquets 25 mm. in diameter and 25 mm. high made up of soils at optimum water content subjected to a pressure of 2,000 lb. per square inch and dried carefully, first in a current of moist air and finally at a temperature of  $110^{\circ}\text{C}$ . The crushing strength of such briquets varies from about 100 lb. to something over 300 lb. per gram of colloid present. It has not been possible,



as yet, to work out a formula or a method for exact determinations of this character, as the strength of the briquet depends upon several factors which cannot at present be evaluated. The strength of the briquet depends upon the pressure, the relative proportion of colloid to non-colloidal material, both of which can be controlled, but it also depends upon the relative proportion of different-sized grains of non-colloidal material, the arrangement or distribution of these different-sized grains, neither of which can be satisfactorily evaluated at present. It also depends upon apparently slight differences in the specific strength of the colloids, upon the determination of the optimum amount of water, and upon whether the colloids are dried at the start or whether they have been dispersed and concentrated without drying. These are matters which require much additional study.

Up to the present time, there seems to be little control over the adsorptive powers and the plasticity, except of a temporary nature, such as may be exerted by coagulating agencies such as lime, so long as they continue present in excess in the soil. The colloidal nature of the material makes it very inactive to any chemical change at ordinary temperatures. The heating of the material above  $110^{\circ}\text{C}$ . requires too much energy for any of our ordinary farm operations. The mixing of sand with plastic clays, as is done in the construction of sand clay roads, appears to be rather an efficient way of diluting and thus controlling the colloidal properties, but is generally too expensive a method to be used in the farming operations. So the permanent control of the very plastic clays by efficient and comparatively cheap methods is as yet entirely unsolved.

The soil colloid, with its large capacity to adsorb water, certain mineral elements, among which particularly are the so-called plant foods, and certain organic bodies constitute the great reservoir for holding in reserve the materials needed for the growth of plants. It gives up water readily to the atmosphere when the latter is below its saturation point and it gives up water readily to colloidal membranes as to seeds and roots, but it holds up to 60 or 70 per cent of water based on the dry weight of the material when subjected to a centrifugal force of 1,000 atmospheres used in the determination of the moisture equivalent of soils.

The adsorption of mineral elements, the separation of the base and acid ions, the relative strength with which the different ions are held or can wander away after their separation, the so-called base exchange, are matters upon which a voluminous literature has been written without revealing much of exact knowledge, because heretofore the soil has been used as a carrier of the colloid. With the separation of the colloid from the soil, which is now possible, investigations of this kind should be more exact and lead to an important field of knowledge where definite laws can probably be worked out.

Colloidal matter in a free state of suspension in water can hardly pass through a fixed colloidal membrane but may mix readily with other mobile forms of colloids and can adsorb many soluble organic compounds and change them to a colloidal form.

Soil colloids in a free suspensoid state, having about 1 g. of solid per 1,000 cc. of water, form a slightly opalescent liquid, the particles of which remain in suspension practically indefinitely in the absence of effective amounts of coagulating materials. Such a solution contains around 100,000 per cent of water, calculated on the basis of the dry weight of the material. As this water evaporates and the colloidal droplets come closer together, they begin to gather in a gel-like mass which slowly subsides. When the water is removed down to from 350 to 600 per cent of the dry weight of the material, the gel has somewhat a consistency of a fruit gel that has set, that is, it holds its shape when taken up in a spoon. From this point on it loses water to the atmosphere until it becomes air-dried, when it becomes hard and brittle like a resin. When these air-dried lumps are reduced to moderately coarse-grained powders, the relations to water are somewhat different. When exposed to a saturated atmosphere under constant temperature, it adsorbs about 30 per cent of water which is given over at  $110^{\circ}\text{C}.$ , and it also contains an additional 10 per cent of water which is only given off at higher temperatures than  $110^{\circ}$ .

The air-dried colloid in a saturated atmosphere carrying 30 per cent water appears dry to the touch, yet molds develop and grow on it readily. When a soil carries its optimum water content, the colloid carries between 35 and 45 per cent of water

which is driven off at 110°C. A colloid with from 35 to 45 per cent of water has the consistency of a heavy wax, which is so stiff that it cannot be kneaded, and fragments cut off with a knife cannot be joined together again by hand pressure. It is probable that in this form the biochemical functions of the soil and the life processes of the plant are at their highest point of efficiency. Where the soil contains an optimum amount of moisture and the colloid has the consistency of a heavy wax it can be worked without danger of puddling or without danger of forming lumps.

When the soil has what is called the "moisture equivalent," that is, when it maintains its moisture content against a centrifugal force of 1,000 gravity, the colloid carries from 60 to 70 per cent of moisture and has the consistency of a fresh American cheese. In this condition it can be kneaded by hand. When the grains of colloid are immersed in water and allowed to take up what it will, it swells about  $3\frac{1}{2}$  times its dry volume and carries about 100 per cent of its dry weight of water. In this condition it is quite soft, and adjacent particles will coalesce with the slightest pressure. In such a condition of saturation a soil carrying a considerable content of colloid cannot be worked without puddling, although, if it is allowed to stand quietly until the water content has been reduced to the optimum, the soil may not suffer any physical injury.

Beyond this 100 per cent of saturation, the lumps of colloid will not take up more water unless under agitation to tear apart the sticky mixture. To get this sticky mass again into a fully suspended state requires a great deal of agitation in order to separate the material into a state of free dispersion.

### CONDITIONS EXISTING IN THE SOIL

Let us now try to picture the state of the colloidal material in arable soils. In the mechanical analysis of soils with a relatively small amount of agitation with an excess of water, the soil falls apart into grains or particles of definite size which are separated into conventional sizes distinguished as different grades of sand, silt, and clay. These analyses can be fairly well duplicated over large areas of the same soil type when one considers

the heterogenous character of the material and the way it has been formed or laid down.

It is now known that about 90 per cent of what has been called the clay group, the particles of which have an upper limit of 5 microns in diameter, consists of colloidal particles and about 10 per cent of unaltered mineral fragments and that this clay group carries about 80 per cent of the total colloidal content of the soil. The average size of the colloidal aggregates in the clay group is estimated at about 2.5 microns in diameter. These colloidal aggregates appear under the ordinary microscope as clean and as sharp in outline as the unaltered mineral fragments, although they do not have the sharp edges and show characteristic differences in the transmission of light. The fact that we obtain consistent results in duplicate analyses indicates that these colloidal aggregates probably existed as such in the soil and that the colloidal material in the soil was not continuous.

Simple mathematical calculations based on the average size, and assuming the particles to be spheres, indicate that in a light sandy soil there will be upward of two billion of these colloidal aggregates per gram of dry soil and that in the heavier clay soils there may be upward of twenty-two to twenty-four billion colloidal aggregates. It has already been pointed out that, when this colloidal material carries an optimum water content of, say, 35 to 45 per cent, it has the consistency of a hard wax that can be readily cut with a knife without shattering and yet so hard that it cannot be kneaded under any ordinary pressure.

It seems probable, therefore, that we have here a fairly correct picture of the mechanical state of the colloid in the soil; that each of these small but independent aggregates has its individual capacity to adsorb its proportion of the water, carry its fair proportion of the colloiddally held potassium, calcium, sodium, and phosphorus, and its proportion of the 3.40 per cent of organic matter, as shown to be present in Table I as the average for the colloids which have been analyzed. Each of these minute particles, therefore, can be looked upon as a culture plate for the growth of bacteria, fungi, and other soil organisms. Instead of plating in agar-agar or in gelatin, as in laboratory investigations, in the soil the plating is done in a matrix formed of the hydrates of silica, alumina, and iron. The soil organisms



obtain from this matrix the organic matter from which they derive their energy of growth and the chemical elements needed to develop their substance or to aid as catalysts in the breaking down of the organic matter.

The average size of the colloidal aggregate is assumed to be about 2.5 microns in diameter. The average diameter of bacteria is around 0.6 of a micron, with 1 or 2 microns for the maximum size. We must conceive, therefore, that a single one of these small culture plates cannot support bacterial growth for any considerable length of time without exhausting the particular kind of organic food which a certain kind of bacteria may demand and without becoming impregnated with the products of bacterial growth which might inhibit their further development until time and conditions had brought about a change. Therefore, it might be expected that, considering any particular aggregate as a culture medium, unless the culture medium was regularly and frequently being supplied with organic food and unless the bacterial growth developed in proper order to maintain a proper balance, the bacterial activities may have to be temporarily suspended while the products of these activities are removed.

It seems a very significant thing that, while we count the culture plates by the billions per gram by the best methods we have been able to devise, we count the bacteria by millions per gram. The textbooks state that the bacterial counts in soils show from 500,000 to 100,000,000 bacteria per gram of soil. These numbers are so far short of the number of culture plates presumably present in the soil that it suggests an analogy with the grazing of cattle or of sheep. In the semi-arid region of the West it may require 10 acres to support a beef animal. In the more humid regions, according to the productivity of the land, it may require from 1 to 3 acres for the support of a dairy cow. In New Jersey an elaborate series of investigations indicates from 5,000,000 to 10,000,000 bacteria on a soil which contains perhaps 10,000,000,000 of these culture plates, indicating that, on the average and under conditions of cropping and manuring, it may require on the average 1,000 culture plates per bacterium.

Under a very intensive system of cultivation, where several crops are grown in the same year and where organic refuse material is applied to the soil every week or two, or in greenhouse

culture, would these culture plates in the soil be maintained in a condition so that, on the average, a much larger number of bacteria could be supported per 1,000 culture plates in the soil?

We must remember that, in addition to the bacteria, there are probably from 80,000 to 14,000,000 fungi and algæ, from a few to as many as 4,500 protozoa per gram of soil, and that, on the average, it is estimated that about 20 per cent of the flora of the soil, as developed on gelatin plates, consists of actinomyces. So we have a very complicated system acting on these minute culture plates in the soil. Furthermore, we must remember that it is not only the number of bacteria but the variety that must be considered. Some are needed to act upon the starches and sugars, a different class seems to be required for the cellulose and woody fibers, others to handle the sulfur compounds, and these different forces must be properly balanced to maintain the soil in a high state of productivity.

Eventually all organic compounds manufactured by the green plants must be broken down to the simple forms of  $\text{CO}_2$  and water to provide the growing plants with  $\text{CO}_2$  to elaborate into new organic compounds in which the energy of the sun can be stored for the maintenance of life and living energy on the earth. At the same time the final destruction of the organic debris must proceed in a certain orderly way so as not to interfere with the activities of growing plants. Man has a certain control over these soil activities through the kind and amount of food supplied the soil, the kind and rotation of crops, through drainage and irrigation, and through cultural methods.

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of the Bureau of Soils on the colloidal material in soils is described in papers by Moore,<sup>9</sup> Whitney,<sup>10</sup> Anderson,<sup>11</sup> Robinson,<sup>12</sup> Davis,<sup>13</sup> Fry,<sup>14</sup> and Gile.<sup>15</sup>

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## CHAPTER XX

### COLLOIDAL PHENOMENA IN METALS AND ALLOYS

By

H. W. GILLETT<sup>1</sup>

While the application of the colloid viewpoint to metals and their alloys is not yet very far advanced, it clarifies our understanding of some facts and may ultimately lead to improved methods of control.

Some overenthusiastic colloid chemists seem inclined to term "colloidal" various phenomena for which the physical chemist has adequate explanation in phase rule relations and other straight physical chemistry, and the application of colloid chemistry to metals would be of doubtful value if it were to lead metallurgists to discard, or to fail to utilize, the tools they already have. As an additional tool, used within reason, colloid chemistry should be of value to the metal industries.

There is difficulty in framing a rigid definition of a colloid or in fixing a sharp boundary between colloidal and non-colloidal phenomena. While a common definition is matter in a state of subdivision such that at least one dimension is very small, say, from molecular dimensions up to  $100\mu\mu$ , that limit cannot be adhered to in respect to metals, for there are obviously colloidal phenomena involving particles which may be visible to the naked eye and are certainly resolvable under the microscope. Then, too, the old conception of a colloid as an essentially and entirely non-crystalline, amorphous material tends to cling and hinders accurate understanding. As a rough definition which will do for present purposes, we might say that any phenomenon depending upon the fact that material is involved which is in so fine a

<sup>1</sup> This chapter is written as a personal, not an official, contribution. It expresses the views of the writer, and not necessarily the official opinion of the Bureau of Mines.



state of subdivision that surface forces play a part which cannot be neglected would be a colloidal phenomenon. That is, the material may be somewhere between the molecular and the massive.

Some applications of well-known colloidal phenomena to metallurgy, such as flotation of ores and precipitation of metallurgical fumes, have been highly developed, but, with molten and solid metals and alloys, colloid chemistry so far chiefly aids as a means of understanding old methods of handling the materials rather than by developing new ones.

The colloid chemistry of metals is handicapped experimentally by the difficulty of observation. Metals are not transparent, so the ultramicroscope is not available. They are good conductors and various electrostatic methods do not apply. They must usually be handled at very high temperatures and the difficulties of control and observation are great. Ordinarily, therefore, we must judge the colloidal conditions obtaining by very indirect evidence.

X-ray spectroscopic methods throw light on some problems, but we lack methods and technique for observation of many colloidal phenomena. Experimental metallurgy carried out from the colloid viewpoint is rare and we are forced to tie up more or less random observations of and facts about metals and alloys with principles of colloid chemistry developed by work on very different materials and at much lower average temperatures. That the correlation is imperfect is to be expected.

#### CRYSTAL SIZE, RATE OF CRYSTALLIZATION, NUCLEI FOR CRYSTALLIZATION

One of the axioms of metallurgy is that the smaller the "grain," or the crystal size, the better and stronger the product. In a cast alloy the crystal size is of great importance and, in an alloy that is later to be forged or rolled, the avoidance of a coarse, dendritic structure is necessary for best results.

Almost the sole method of control of crystal size in a given alloy rests in the rate at which freezing is allowed to take place. Rapid freezing gives small crystals, slow freezing large ones.

The pouring temperature, the volume of the casting, the heat capacity and heat conductivity of the mold, all affect the rate of freezing. A small casting poured at the lowest possible temperature with a chill mold will usually give a product which is vastly better than can be obtained under conditions which do not allow rapid freezing. This condition is very noticeable in cast aluminum alloys,<sup>2</sup> in which hot pouring gives weak castings and heavy sections slow to freeze are far less strong per unit area than thin sections which freeze quickly.

Zinc, chill cast, may give around 20,000 lbs. per sq. in. tensile strength, while if it is cooled slowly, the strength may be under 5,000. The lower the melting point of the alloy the more noticeable is the effect of slow cooling, generally speaking.

The composition of the alloy alters the thermal conductivity and, hence, changes the freezing rate directly. But the grain size varies with composition more than can be accounted for by such factors. A little cadmium reduces the grain size of zinc very markedly. There seems to be a variation in the number of centers or nuclei of crystallization. The greater the number of nuclei, the finer the grain. Hoyt<sup>3</sup> discusses the subject of nuclei number and crystallization velocity in some detail.

It is possible that colloid phenomena play a part in the formation of nuclei. Quincke<sup>4</sup> put forth the theory that, as a metal approaches its freezing point, it takes the form of a foam, many cells being formed, which, in a pure metal at least, have the same composition at the walls as in the interior. When this foam freezes, the cells are postulated to be perpetuated as the "grains" of the metal. But Desch<sup>5</sup> was unable to substantiate this theory experimentally.

<sup>2</sup> GILLET, H. W.: Influence of pouring temperature on aluminum alloys, 8th Int. Cong. App. Chem. (1912), sec. II, Orig. Comm. 2, p. 105, *Metal Ind.*, **11** (1913), 167.

<sup>3</sup> "Metallography," pt. I., Principles, 1920, p. 102.

<sup>4</sup> Foam structure of metals, *Int. J. Met.*, **4** (1913), 23, 79, 303.

See also BEILBY, G. T.: The solidification of metals from the liquid state, *J. (Brit.) Inst. Met.*, **8** (1912), no. 2, 186.

<sup>5</sup> Solidification of metals from the liquid state, 1st Rept., *J. (Brit.) Inst. Metals*, **11** (1914), no. 1, 57. Also, The solidification of metals from the liquid state, 2nd Rept., *J. (Brit.) Inst. Metals*, **22** (1919), no. 2, 241.

Alexander<sup>6</sup> considers that, as the metal approaches the freezing point, it becomes an isocolloid, that is, the molecules begin to arrange themselves regularly in an approach to the orientation of the solid crystal and that the groups of molecules thus arranged are suspended in unoriented liquid. Each separate group would then become a nucleus, and the more rapid the cooling the less the chance for two nuclei to join up and the greater the chance that each one will separately draw upon the liquid to complete its crystalline arrangement.

An analogous case to crystallization from liquid solution is the formation of crystals of another phase from a solid solution, as occurs when austenite is cooled through its critical range. According to Giolitti,<sup>7</sup> titanium and vanadium have a specific action in supplying or causing the formation of large numbers of nuclei for crystallization in the particular case of austenite.

Saklatwalla<sup>8</sup> points out that the sets of atoms which happen to have an arrangement in the liquid, corresponding with the space lattice arrangement in the solid crystal, will act as nuclei for crystal growth. This means that the laws of chance, rather than colloid principles, govern.

On the whole, the colloid viewpoint has not yet thrown much light on the mystery attending the birth of a crystal, nor has it yet shown how to increase the number of nuclei and produce a finer grained metal.

### INTERFERENCE WITH CRYSTALLIZATION

In the alloys of aluminum and silicon it is found that, whereas the straight aluminum-silicon alloy made by melting together aluminum and silicon has a eutectic composition of about 11 per cent silicon, one made with the addition of 0.02 of 1 per cent of sodium (most of which burns out, leaving only the faintest trace of sodium in the final alloy) has a eutectic composition of

<sup>6</sup> Colloidal state in metals and alloys, *Chem. Met. Eng.*, **26** (1922), 54, 119, 170, 201.

<sup>7</sup> "Heat Treatment of Soft and Medium Steels," translated by THUM, E. E. and VERNACI, D. G., 1921, p. 243.

<sup>8</sup> Inherent effect of alloying elements in steel, *Trans. Am. Electrochem. Soc.*, **43** (1923), 137.

about 15 per cent silicon, and the structure of the second or "modified" type of alloy is much finer than in the first or normal type, the silicon being in such a fine state of subdivision as to be scarcely resolvable under the microscope. The aluminum-silicon and the aluminum-silicon-copper alloys show less contraction on freezing than other aluminum alloys and, hence, have superior casting properties. Their strength and lightness make them of great value.<sup>9</sup>

The peculiar action of sodium in modifying the alloy is ascribed by Jeffries to the insolubility of the sodium and to its precipitation in the melt in the shape of fine globules of colloidal size which are postulated to interfere with the normal crystal growth of the aluminum-silicon alloy, and, hence, to allow undercooling which, in turn, promotes the formation of small crystals. Since the sodium will still be liquid when the alloy freezes, it is necessary to consider the action as obstruction to grain growth rather than as the supplying of nuclei for crystallization.

Cain<sup>10</sup> says, "The influence of sodium in dispersing the silicon is so profound that one is tempted to look upon it as a peptizer and the ultimate alloy as a colloid."

Edwards<sup>11</sup> finds that the addition of antimony or bismuth to the aluminum-silicon alloys modified with sodium has a beneficial effect.

Such a displacement of equilibrium is very rare, and, if the explanation is correct, the phenomenon opens up possibilities for application to other alloys.

Saklatwalla<sup>12</sup> postulates that adsorption may differ on different crystal faces, and the adsorption of impurities or of other

<sup>9</sup> JEFFRIES, Z.: Aluminum silicon alloys, *Chem. Met. Eng.*, **26** (1922), 750; Discussion, Feb., 1923, meeting, Am. Inst. Min. Met. Eng., *Chem. Met. Eng.*, **28** (1923), 392; EDWARDS, J. D.: Properties and manufacture of aluminum-silicon alloys, *Ibid.*, **27** (1922), 654; also Thermal properties of aluminum silicon alloys, *Ibid.*, **28** (1923), 165; CURRAN, J. J.: "Modification" of aluminum-silicon alloys, *Ibid.*, **27** (1922), 360; DIX, E. H., JR. and LYON, H. J.: Copper-silicon-aluminum alloys, *Trans. Am. Soc. Test. Materials*, **22** (1922) 250; *Foundry*, **51** (1923), 331.

<sup>10</sup> Some new and important alloys of aluminum, *Metal Ind.* (London), **20** (1923), 413.

<sup>11</sup> EDWARDS, J. D.: U. S. Pat. 1453928, May 1, 1923.

<sup>12</sup> *Loc. cit.*



elements present may thus alter the velocity of crystallization in some directions and produce a dendritic structure instead of a fine-grained one. Smalley<sup>13</sup> suggests that graphite is suspended in the melt in gray iron and that the effect of special added elements is largely as coagulating or peptizing agents, thus controlling the distribution of graphite on freezing. But this point of view is not upheld by the equilibrium diagram.

Molten metals dissolve gas, and, instead of dissolving less at higher temperatures, as is the case with other liquids, the solubility increases with the temperature. As the metal cools, gas is released in bubbles and these may be caught as the metal freezes and produce unsoundness. Certain additions, such as manganese, silicon, titanium, aluminum, etc., appear to increase the solubility of the gas and prevent it from coming off in bubbles when the metal freezes.

Whether this is a problem of true molecular solution or some sort of adsorption is not yet clear. At any rate, the retention of gas bubbles by the molten or pasty material is closely analogous to a colloidal phenomenon.<sup>14</sup>

#### "SONIMS"

All commercial metals and alloys contain more or less matter foreign to the desired composition. This foreign material appears in the solid metal as "dross," "inclusions," or "sonims" (solid, non-metallic impurities). Alumina in aluminum alloys, zinc oxide in brass, stannic oxide in bronze, and sulfides and slag in steel are examples. These examples are cases where the included material is probably practically insoluble in the molten as well as in the solid metal.

The evidence as to solubility of sulfides in molten iron and steel is contradictory and confusing, while there is pretty good evidence that some slags (oxide mixtures, including silicates) may have a slight true solubility, though it is evidently very limited. In the case of cuprous oxide in copper (and probably of ferrous oxide in iron), the oxide is soluble in the liquid but insoluble in the solid. These cases have to be handled by chemical methods of elimination of the oxide.

<sup>13</sup> Special cast iron, *Met. Ind.* (London), **22** (1923), 36.

<sup>14</sup> ANON.: Blowholes in steel castings, *Metal Ind.* (London), **22** (1923), 108.

But when the included material is insoluble in the melt, or as far as it is present in excess of its solubility, the emulsion or suspension is a plain case of a colloidal phenomenon. Although much of the suspended material is of a size sufficient to be readily visible under the microscope, a good deal of it is barely visible, and nobody knows how much is present which is not resolved under the microscope. Although much of this material is too large to class as colloidal according to the usual statements of limiting size, under the conditions of temperature and viscosity obtaining, it is nevertheless small enough so that surface forces play a large part.

There is a certain limiting size above which the solid or liquid impurities rise rapidly from the melt as dross or slag, or, in case they are heavier than the melt, sink rapidly. If the impurities agglomerate or coalesce so as to exceed the limiting size, they are eliminated on standing.

Upton<sup>15</sup> has dealt in as quantitative a manner as the data available will allow with the analogous case of the fall of raindrops in air; a drop of 0.01 in. diameter will fall about  $6\frac{1}{2}$  ft. per second, one of 0.001 in. about 38 ft. per hour, while one of 0.0001 in. will fall only about  $4\frac{1}{2}$  in. per hour. The rising of inclusions in steel, for example, cannot be calculated very closely, since we lack data for viscosity and specific gravity of molten metal, slag, etc., but the effect of difference in size will be even more marked than in the case of the raindrops.

Particles below the limiting size remain suspended, and the problem of getting clean metal is a problem of coalescence or agglomeration, *i.e.*, the breaking up of the emulsion or suspension. Present methods of securing clean metal rely almost wholly on a gravity separation, like that of cream from milk, by allowing the molten metal to stay quiet for a considerable period. Crucible and electric melting allow this to a greater extent than open-hearth or converter melting, and, with similar raw materials and the same final analysis (as analyses are ordinarily made), the methods that allow the better elimination of the sonims give the better steel.

Excessive amounts of suspended matter probably increase the tendency to a coarse, dendritic structure, and certainly

<sup>15</sup> Raindrops and Engineering, *Sibley J. Eng.*, **37** (1923), 5.

increase the difficulty of destroying this structure by heat treatment. The evil effects of sonims vary with their size and nature. In wrought materials an impurity which is plastic at the temperature at which the metal is worked will roll, draw, or forge out into rods or plates which give the material a fiber something like that of wood. These inclusions are sometimes advantageous and intentional, as in the case of screw stock, where the presence of considerable manganese sulfide is wanted to allow the chips to break up and facilitate machining. Ordinarily, the inclusions are undesirable. They may be relatively harmless in a piece which, in service, is stressed along the direction in which the inclusions are elongated, but serious or even fatal when the piece is stressed across the fiber.<sup>16</sup>

To these inclusions are primarily due the woody fiber of transverse test pieces and the poor ductility and resistance to shock of transversely cut bars. In resistance to "fatigue,"<sup>17</sup> i.e., to repeated stress, transverse bars of material with drawn-out inclusions are decidedly inferior. This is due to the inclusion acting as an "internal notch,"<sup>18</sup> which increases the local stress at the inclusion over that calculated from the dimensions of the piece and used as the basis of engineering design. A large propor-

<sup>16</sup> PRIESTLEY, W. J.: Effect of sulphur and oxide in ordnance steel, *Trans. Am. Inst. Min. Met. Eng.*, **67** (1922), 317; BREARLEY, H.: 1st Report Gas Cylinders Research Comm., Dept. Sci. and Indust. Res., London, 1921, appendix 5, pt. 3; AITCHISON, L.: Die blocks, *Drop Forger*, Birmingham, Eng., **1**, No. 2 (1921); quoted in *Forging and heat treating*, **8** (1922), 36; GIOLITTI, F.: *Loc. cit.*, p. 243.

<sup>17</sup> MOORE, H. F. and KOMMERS, J. B.: An investigation of the fatigue of metals, *Bull.* 124, Eng. Expt. Sta., Univ. of Ill. *Bull.* 19 (1921), no. 8, p. 134. McADAM, D. J.: Endurance properties of steel, *Proc. Am. Soc. Test. Materials*, **23** (1923). HAIGH, R. P.: Elastic and fatigue limits in metals, Lecture Nov. 9, 1922, before Birmingham Metallurgical Soc. Abstracted in *Metal Ind.* (London), **21** (1922), 466; LEA, F. C.: The effect of repetition stresses on materials, *Engineering* (London), **115** (1923), 217, 252.

<sup>18</sup> INGLIS, C. E.: Stresses in a plate due to the presence of cracks and sharp corners, *Trans. Inst. Naval Arch.*, **55** (1913), pt. 1, 219; GRIFFITH, A. A.: Phenomena of rupture and flow in solids, *Trans. Roy. Soc., Series A*, **221** (1920), 163; COKER, E. G.: Photo elastic measurements of stress distribution, *Minutes Proc. Inst. Civil Eng.*, **208** (1918-1919), pt. 2, 362; *Chem. Met. Eng.*, **25** (1921), 714; *Engineering*, **112** (1921), 81; *Trans. Inst. Naval Arch.*, **55** (1913), pt. 1, 207; MATHEWS, J. A.: Discussion of Hoyt, S. L., "Static, dynamic and notch toughness," *Trans. Am. Inst. Min. Met. Eng.*, **62** (1920), 490; GIOLITTI, F.: *Loc. cit.*, pp. 141, 283, 360.



tion of failures of metals in service,<sup>19</sup> particularly in automobiles and aircraft, is traceable to dirty metal, and the reliability of high-speed machinery is a function of the thoroughness of the coalescence and elimination of the emulsified non-metallic impurities.

The recent book by Giolitti<sup>20</sup> deals almost entirely with the difficulties encountered in handling steel due to inclusions and the resulting dendritic structure and with the colloidal phenomena involved. Various other writers<sup>21</sup> recognize that the problem of inclusions is one of the breaking up of a colloidal suspension.

Bancroft<sup>22</sup> suggests that, besides the present method of gravity separation, other methods of inducing agglomeration of the sonims or of adsorbing them in added materials might be of

<sup>19</sup> ROSENHAIN, W.: "Introduction to Physical Metallurgy," 1915, pp. 153-318; McCANCE, A.: Non-metallic inclusions, their constitution and occurrence in steel, *J. Brit. Iron Steel Inst.*, **97** (1918), no. 1, 239; BARBA, W. F. and HOWE, H. M.: Acid open-hearth process for manufacture of gun steels and fine steels, *Trans. Am. Inst. Min. Met. Eng.*, **67** (1922), 172; STROUGHTON, B.: "Metallurgy of Iron and Steel," 1911, p. 168; HOYT, S. L.: "Metallography," pt. 2, 1921, pp. 261, 265-276. See also Manganese, *Bur. Mines Bull.* 173 (1920), chap. 11, 196; LANGENBERG, F. C.: Reports of tests of metals at Watertown Arsenal during 1918, *War Dept. Doc.* no. 901 (1919), 57, 64, 66; BOYNTON, H. C.: Discussion—Symposium on flaky steel, *Trans. Am. Inst. Min. Met. Eng.*, **69** (1920), 279; FREMONT, C.: Alternating stresses, *Compt. rend.* **168** (1919), 54; *J. Brit. Inst. Metals*, **21** (1919), 469; PHILPOT, H. P.: Shop practice in respect to aircraft steel, *Aeronautical J.*, **23** (1919), 112; KNERR, H. C.: Remarks on fatigue failure of metal parts, *Forging and Heat Treatment*, **8** (1922), 40; ROLFE, R. T.: The testing of materials, *Metal Industry* (London), **20** (1922), 367; JOHNSON, J. B. and DANIELS, S.: Study of some failures in aircraft engine and plane parts, *Trans. Am. Soc. for Steel Treating*, **2** (1922), 1167; MATHEWS, J. A.: The electric furnace in refining iron and steel, *Iron Age*, **110** (1922), 1127; *Chem. Met. Eng.*, **27** (1922), 872; Dirty steel (editorial), *Chem. Met. Eng.*, **28** (1923), 51.

<sup>20</sup> GIOLITTI, F.: "Heat Treatment of Soft and Medium Steels," 1921, translated by Thum, E. E. and Vernaci, D. G., pp. 123, 133, 135.

<sup>21</sup> HIBBARD, H.: *Trans. Am. Inst. Min. Met. Eng.*, **41** (1910), 803; CONARROE, A. N.: Heat treatment of steel castings, *Foundry*, **48** (1920), 598; The thermal treatment of cast steel, *Trans. Am. Soc. for Steel Treating*, **1** (1921), 746; GILLETT, H. W.: Emulsions and suspensions in molten metals, *J. Ind. Eng. Chem.*, **9** (1917), 31.

<sup>22</sup> Cited by GILLETT, H. W., "Application of colloid chemistry to production of clean steel," *Trans. Am. Inst. Min. Met. Eng.*, **69** (1923), 768.



service. He also points out that the suspension of non-metallic particles in metals is the reverse case of the phenomenon found in electrolysis of molten salts of metals, where the metal may be peptized and remain suspended as a "metal fog."

### RETENTION OF METAL BY SLAGS AND MATTES

Another case where metal is the dispersed phase and is suspended in non-metallic material occurs in the retention of metal globules or shot by slags or mattes in smelting and refining processes. A sharp separation of metal is highly important for the economical working of many such processes.

### COALESCENCE

Other cases of the dispersion of metal globules occur in "floured" or "sickened" mercury,<sup>23</sup> where the globules are covered with a coating which prevents coalescence, and in the remelting of dirty aluminum chips. When aluminum chips<sup>24</sup> are covered with oxide or dirt, each tiny chip melts to a globule, the surface of which is covered with adsorbed foreign material, and, unless the weight of the globule is sufficiently great, it will not break through this skin and come into metallic contact with its fellows, but will remain separate and not be recovered in the melting. It is necessary to dissolve or adsorb the coating in some flux or else to apply mechanical puddling to break through the skin. Without such precautions a recovery of less than 50 per cent of the metallic content of dirty chips is often made on remelting, while similar chips that are clean or are properly fluxed or puddled may give a recovery of 90 per cent.

The melting of "blue powder,"<sup>25</sup> finely divided zinc covered with oxide or other foreign material, presents a similar problem

<sup>23</sup> GOWLAND, W.: "Metallurgy of the Non-ferrous Metals," 1914, p. 305.

<sup>24</sup> GILLETT, H. W. and JAMES, G. M.: Melting aluminum chips, U. S. Bur. Mines Bull. 108 (1916).

<sup>25</sup> ROEBER, E. F.: Editorial, *Met. Chem. Eng.*, **10** (1912), 451; HANSEN, C. A.: Discussion, *Trans. Am. Electrochem. Soc.*, **24** (1913), 138; INGALLS, W. R.: The electric melting of zinc ore, *Chem. Met. Eng.*, **10** (1912), 482; Blue powder in zinc smelting, *Min. Met. Eng.*, no. 184 (Apr., 1922), 13; "The Metallurgy of Zinc and Cadmium," (1903), pp. 205, 529; JOHNSON, W.:

and the avoidance of its production, and its remelting when it is produced, are great difficulties in zinc smelting, particularly in electrothermal processes.

A little tin oxide in a fusible boiler plug<sup>26</sup> may similarly prevent coalescence, prevent the blowing out of the plug, and cause fatal boiler explosions.

In the "calorizing" process, in which iron or steel is coated with aluminum<sup>27</sup> by being heated in contact with aluminum powder at temperatures above the melting point of aluminum, aluminum oxide is mixed with the aluminum powder in order to prevent coalescence.

In "sherardizing," it is not desired that the zinc dust or blue powder used should coalesce,<sup>28</sup> and a certain oxide content is usually considered necessary, although, since sherardizing is normally carried out at temperatures below the melting point of zinc, the case is not exactly analogous to calorizing. But in the Sang process,<sup>29</sup> in which temperatures above the melting point are used, the case is analogous.

### ELECTROPLATING

In electroplating and electrolytic refining, most metals tend to give non-adherent or "treed" deposits, especially at high current densities. Traces of some "addition agent," usually an organic colloid, such as glue, which is adsorbed by the cathode,

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The art of electric zinc smelting, *Trans. Am. Electrochem. Soc.*, **24** (1913), 191; *Chem. Met. Eng.*, **13** (1915), 763; LYON, D. A. and KEENEY, R. M.: Possible application of the electric furnace to western metallurgy, *Trans. Am. Electrochem Soc.*, **24** (1913), 138; BLEEKER, W. F.: An electrolytic method for the reduction of blue powder, *Trans. Am. Electrochem. Soc.*, **21** (1912), 359; BILLAZ, A.: Zinc dust and its uses, *Chem. Met. Eng.*, **28** (1923), 644.

<sup>26</sup> BURGESS, G. K. and MERICA, P. D.: Investigation of fusible-tin boiler plugs, U. S. Bur. Standards. *Tech. Paper* 53 (1915); *Trans. Am. Inst. Metals*, **9** (1915), 21.

<sup>27</sup> RUDER, W. E.: Calorizing metals, *Trans. Am. Electrochem. Soc.*, **27** (1915), 254.

<sup>28</sup> TROOD, S.: Sherardizing, *Trans. Am. Inst. Metals*, **9** (1915), 101.

<sup>29</sup> SANG, A.: Galvanizing wire in zinc dust, *Trans. Am. Electrochem. Soc.*, **20** (1911), 259.

produce finer crystals and give smooth, adherent deposits.<sup>30</sup> Conversely, in electrolytic analysis, the adsorption of weighable amounts of such materials from the bath must be guarded against. The adsorbed material need not be a colloid.<sup>31</sup>

### ADSORPTION

The property of metals and alloys by which gases and liquids are adsorbed in the surface plays a large rôle in the use of metals as contact catalytic agents<sup>32</sup> and as bearing metals.

The chief duty of a bearing metal is nowadays considered to be its ability to adsorb a film of the lubricant and prevent metal-to-metal contact. Certain groups of atoms of the lubricant seem to find a toe-hold in the space lattice of the bearing metal.<sup>33</sup>

If and when the supply of lubricating oil gives out, search may have to be made among materials not now used as lubricants and alloys not now used as bearing metals on the basis of their mutual ability for and of adsorption.

The precipitation of gold and silver by charcoal, which is being studied by the Reno, Nevada, Station of the Bureau of Mines, is another metallurgical application of adsorption.

### CORROSION

The corrosion of metals and alloys depends very largely on whether or not a protecting film of colloidal thickness forms on the surface, and on whether or not this film is self-healing.<sup>34</sup>

<sup>30</sup> SAND, H. J. S.: The rôle of colloids in electrolytic metal deposition, Fourth Report on Colloid Chemistry and Its General and Industrial Applications, *Brit. Assoc. Adv. Sci.* (with bibliography), 1922, p. 346.

<sup>31</sup> BANCROFT, W. D.: Colloid chemistry and electrochemistry, *Trans. Am. Electrochem. Soc.*, **37** (1920), 55; KOLSCHÜTTER, V.: Colloidal chemistry and electrochemistry, *Kolloid-Z.*, **31** (1922), 263.

<sup>32</sup> BANCROFT, W. D.: Theory of contact catalysis, *Trans. Am. Electrochem. Soc.*, **32** (1917), 475; The poisoning of catalytic agents, *Trans. Am. Electrochem. Soc.*, **32** (1917), 439.

<sup>33</sup> DUNSTAN, A. E. and THOLE, F. B.: Our broadening knowledge of lubrication, *Chem. Met. Eng.*, **28** (1923), 299; BINGHAM, E. C.: "Fluidity and Plasticity," 1922, chap. XI.

<sup>34</sup> BANCROFT, W. D.: Problems of retarding corrosion, *Raw Materials*, **5** (1922), 267.

Passivity of metals and formation of electrolytic "valves" and rectifiers are related to such films.

Colloidal phenomena and colloid products of corrosion play a large part in some theories of corrosion.<sup>35</sup>

The literature is too voluminous for any save brief reference here, and the whole subject is controversial. It is certain, however, that colloidal phenomena of corrosion cannot be disregarded.

### "AMORPHOUS" METAL HYPOTHESIS

Few theories in metallurgy have been more discussed or more widely used than the hypothesis of Beilby,<sup>36</sup> elaborated by Rosenhain and others,<sup>37</sup> in regard to "amorphous" metal. Beilby noted that on polishing a metal so that its surface flows by plastic deformation, this surface skin differs in properties, especially in hardness, from massive metal not so deformed. It is obvious that plastic deformation breaks the original crystals down, producing very fine fragments or debris. Such fragments, as every colloid chemist knows, may have surface forces great enough to show a marked effect, whereas the surface forces of the massive original material may have been negligible. It is fair enough to classify this very fine material as a colloid solely from its state of subdivision. The attraction between the subdivided units keeps the material in solid form, that is, it is not a powder, but remains attached to the original crystalline material, but there

<sup>35</sup> FRIEND, J. N.: A new theory of the corrosion of iron, *Trans. Am. Electrochem. Soc.*, **40** (1921), 63; Symposium on corrosion of metals, *Trans. Faraday Soc.*, **11** (1916); Corrosion symposium, *Trans. Am. Electrochem. Soc.*, **39** (1921), 53; BENGOUGH, G. D. and STUART, J. M.: Colloids in corrosion, Sixth Report of the Corrosion Research Comm., *J. (Brit.) Inst. Metals*, **38** (1922), no. 2, 31; SAKLATAWALLA, B. D.: Adsorption a criterion of corrosion, *Chem. Met. Eng.*, **27** (1922), 647; SHAW, W. R. D.: Practical and theoretical aspects of corrosion, *Beama*, **12** (1923), 272.

<sup>36</sup> BEILBY, G. T.: The hard and soft states in metals, *J. (Brit.) Inst. Met.*, **6** (1911), no. 2, 5; BEILBY, G. T.: quoted by Howe, H. M.: "Metallography of Steel and Cast Iron," 1916, 374; THORPE, E.: *Dict. of Applied Chemistry*, **4** (1923), 299.

<sup>37</sup> ROSENHAIN, W.: "Introduction to the Study of Physical Metallurgy," 1915, p. 246; BENGOUGH, G. D.: A study of the properties of alloys at high temperatures, *J. (Brit.) Inst. Met.*, **7** (1912), no. 1, 123.



is an obvious effect of subdivision. Cold-worked metals or alloys, such as those subjected to cold-rolling, drawing, forging, spinning, etc., have their properties altered, and altered in the direction in which we find the properties to go as we go from coarsely crystalline to more finely crystalline material.

But Beilby, unfortunately, did not utilize the modern colloid viewpoint, in which size and surface forces are considered predominant, and, instead of calling the subdivided, shattered, slipped, and distorted material a colloid, he considered that the shattering had entirely destroyed the regular crystalline arrangement of some of the molecules and produced a material that was truly amorphous and analogous to glass or pitch.

The next step postulated that not only did amorphous material exist in worked metals, but that, between the crystals of a cast, unworked metal or alloy, there was an unoriented layer, or amorphous undercooled liquid. This pitch-like material between the crystals is then considered as a cement. Had the proponents of the hypothesis been willing to be satisfied with arguing that at a point of contact of two crystals the fields of force that determine the arrangement of the molecules in the space lattice and in the crystals extend beyond the individual crystal, so that the outer layer or layers of molecules are directioned, not by a single field of force, but by the resultant of two (or more) such fields—resulting in surface conditions, surface energy, and surface forces different from the conditions of energy and forces in the body of the crystal—little objection could be raised to the theory. And, in fact, the prestige of its originators was so great that the theory was widely accepted, even in the face of knowledge that the crystallizing forces in metals and alloys are so great that a non-crystalline metal or alloy has never been seen and can with difficulty be conceived. But amorphous, supercooled liquid

<sup>38</sup> JEFFRIES, Z. and ARCHER, R. S.: Slip interference theory of the hardening of metals, *Chem. Met. Eng.*, **24** (1921), 1057; WESTGREN, A. (also quotation from Benedicks, C.): Discussion of above, *Ibid.*, **25** (1922), 641; JOHNSON, F.: The theory of hardening, *Met. Ind.* (London), **22** (1923), 34; MARK, H., POLANYE, E. M. and SCHEED, E.: Processes in the stretching of microcrystals, *Z. Physik.*, **12** (1922), 58, 78, 111; HUMFREY, J. C. W.: Internal stresses in relation to microstructure, *Trans. Faraday Soc.*, **17** (1921), 47.

films of a thickness of some thousand to a hundred molecules were postulated in the early days of the theory.

Most alloys, broken at low temperatures, fracture through the crystals and not between them. There are planes of easy slip<sup>38</sup> in crystals, corresponding to certain planes of the space lattice, on which movement is not much hindered.

In a coarsely crystalline material, these planes extend through considerable space, so that a fracture started in one crystal finds little resistance and a crack can start readily. In a finely crystalline material, an incipient crack in one crystal more promptly runs up against another crystal in which the plane of weakness is at such an angle to the crack that the crack cannot so readily propagate.

In metals at low temperatures, the fracture then avoids the boundaries of the crystals. At some higher temperatures, however, the fracture is no longer through the crystals, but between them, and the strength falls off rapidly with increase of temperature. If we wish to postulate a weakening of the surface forces with increasing temperature at a greater rate than of the internal cohesion of the crystals at the slip planes,<sup>39</sup> this phenomenon is understandable, and such conception does not involve the hypothesis of an undercooled liquid and, hence, is not incompatible with the crystalline nature of metals and alloys.

Mark<sup>40</sup> and co-workers show by X-ray spectroscopic examination that, as certain metals are plastically deformed, the orientation of the space lattices changes so that the slip planes lie at a definite angle to the line of application of force. When this angle becomes small and reaches a definite value, ductility is lost and brittleness ensues. The angle varies with the temperature, so that the amorphous hypothesis is not the only explanation for the effect of temperature.

The mechanical conception of crystals stuck together by a pitch-like cement, which is harder and stronger than the crystal at low temperatures, and weaker and more plastic or fluid at higher temperatures, fitted in so well with the phenomenon of

<sup>39</sup> JOHNSON, F.: The theory of hardening, *Met. Ind.* (London), **22** (1923), 34.

<sup>40</sup> MARK, H., POLANYE, E. M. and SCHEED, E.: Processes in the stretching of microcrystals, *Z. Physik.*, **12** (1922), 58, 78, 111.

low-temperature fracture through, and high-temperature fracture between, the crystals, that the theory gained wide acceptance, and it does serve as a convenient shorthand to recall to the memory the varying types of fractures.

But nobody has yet produced a specimen of orthodox metal or alloy that is completely amorphous, and the postulated thickness of the amorphous layer is below the limit of microscopic resolvability. The amorphous material is, therefore, merely an unproved assumption. Rosenhain<sup>41</sup> has prepared an alloy (ternary eutectic of zinc, copper, and aluminum), which, after rolling, shows at low temperatures some of the properties ascribed to amorphous metal, and which Rosenhain thinks may contain as much as 20 per cent of amorphous material. Hatfield<sup>42</sup> points out that the application of the amorphous theory to this alloy is not conclusive, and Jeffries<sup>43</sup> (who in his earlier publications appeared to accept the amorphous hypothesis bodily, but who now finds much of it untenable) ascribes the properties of the alloy to a very fine grain size. Since amorphous metal cannot be isolated or seen, one can ascribe to it any properties one likes without fear of disproof. The amorphous cement has, therefore, been made a convenient means for the explanation of any phenomenon that was not clear, and, instead of thinking the problem through and experimenting further, many investigators and writers refer observed phenomena of the most varying nature to the amorphous cement.

X-ray examination<sup>44</sup> shows that colloidal gold and silver are not amorphous but of definitely crystalline orientation, and even

<sup>41</sup> ROSENHAIN, W., HAUGHTON, J. L. and BINGHAM, K. E.: Zinc alloys with aluminum and copper, *J. (Brit.) Inst. Met.*, **23** (1920), no. 1, 261.

<sup>42</sup> HATFIELD, W. H.: Discussion, *J. (Brit.) Inst. Met.*, **23** (1920), no. 1, 318; also The mechanism of the failure of metals from internal stress, *Trans. Faraday Soc.*, **17** (1921), 36; see also HEYN, E.: Einige Fragen aus dem Gebiet der Metallforschung, *Metall u. Erz.*, **6** (1918), 411, 436; see also SAKLATAWALLA, B. D.: Inherent effect of alloying elements in steel, *Trans. Am. Electrochem. Soc.*, **43** (1923), 137.

<sup>43</sup> JEFFRIES, Z. and ARCHER, R. S.: The amorphous metal hypothesis, *Chem. Met. Eng.*, **25** (1921), 697.

<sup>44</sup> SCHERRER, P.: Estimation of the size and internal structure of colloidal particles by means of Röntgen rays, *Nach. Ges. Wiss., Gottingen* (1918), 96; *J. Chem. Ind.*, **116** (1919); *Chem. Abs.*, 274.

"amorphous" silicon<sup>45</sup> has also been shown to be crystalline. Jeffries<sup>46</sup> shows that Beilby's original hypothesis in regard to hardening is impossible and that the amorphous theory is not of quantitative, though it may be of qualitative, value.

The weight of evidence seems to indicate that the alleged presence of an undercooled liquid in metals and alloys is a myth, and such a prominent colloid chemist as Bancroft<sup>47</sup> wholly repudiates the presence of this liquid.

Alexander<sup>48</sup> does not admit the alleged lack of orientation in the hypothetical material. Besides the colloid chemists, a good many eminent metallurgists, though probably a minority, do not accept the amorphous hypothesis completely, if at all. But, with Jeffries, the colloid chemists and a good many metallurgists appear to regard the phenomena, formerly explained by the amorphous cement theory, as due to very fine, crystalline material, of colloidal dimensions and, hence, of great surface forces.

### HARDENING

The old amorphous theory called for the formation of amorphous material on cold-working, which was harder than the crystal, though there is no obvious reason for assuming that an undercooled liquid would be harder than the same material in the crystalline state. When experimental evidence had accumulated that made it impossible to retain this as an adequate theory of hardening, Jeffries and Archer<sup>49</sup> developed the "slip-interference" theory of hardening, part of which refers to the external support afforded a fracturing grain when it meets a differently oriented grain, which is in accord with the observed properties of fine-grained *vs.* coarse-grained material. Another part of the theory involves the "keying" of slip planes by small projecting particles of colloidal size.

<sup>45</sup> MANCHOT, W.: Identity of amorphous and crystalline silicon, *Z. anorg. allgem. Chem.*, **124** (1922), 333.

<sup>46</sup> JEFFRIES, Z. and ARCHER, R. S.: The properties of cold-worked metals, *Chem. Met. Eng.*, **27** (1922), 882; see also *Chem. Met. Eng.*, **25**, 703.

<sup>47</sup> Colloid chemistry and metallurgy, *Trans. Am Inst. Min. Met. Eng.*, **63** (1922), 604.

<sup>48</sup> Colloidal state in metals and alloys, *Chem. Met. Eng.*, **26** (1922), 122.

<sup>49</sup> Slip interference theory of the hardening of metals, *Chem. Met. Eng.*, **24** (1921), 1057.



Merica<sup>50</sup> points out that in certain cases of solid solutions where there is no obvious or probable presence of colloidal particles, but the atoms of the alloying metal are regularly arranged in relation to the atoms of the alloyed metal, the keying theory is inadequate and suggests that the presence of the "stranger" atom distorts the space lattice and disturbs the atomic forces acting between the molecule containing the stranger atom and surrounding molecules.

Rosenhain<sup>51</sup> later elaborated this theory and, since it is experimentally borne out by X-ray data, it is becoming accepted as the explanation of hardening of solid solutions. Such cases appear to be molecular phenomena, not colloidal.

But colloidal phenomena do come into play in the hardening of such materials as steel by quenching and duralumin by aging, and in these cases the slip interference theory outlined by Merica<sup>52</sup> and elaborated by Jeffries and Archer is of interest and value. For years discussion has raged about the nature of martensite and many theories have been evolved to explain the metallographic constituents martensite and troostite, for which there is no place on the equilibrium diagram and which are metastable transition stages. Until colloidal principles were invoked there was no satisfactory explanation of the observed facts and no theory unassailable or unassailed.

In duralumin, at temperatures somewhat above 500°C., we have a homogeneous solid solution of the compounds  $\text{CuAl}_2$  and  $\text{Mg}_2\text{Si}$  in aluminum. As the temperature falls, the equilibrium diagram (established by long annealing of specimens) shows that  $\text{CuAl}_2$  and  $\text{Mg}_2\text{Si}$  become less soluble<sup>53</sup> and are

<sup>50</sup> A discussion of the slip-interference theory of hardening, *Chem. Met. Eng.*, **26** (1922), 881.

<sup>51</sup> Second Institute of Metals, Lecture—Solid solutions, *Brass World*, **19** (1923), 71; *Trans. Am. Inst. Min. Met. Eng.*, **69** (1923), 1003. The hardness of solid solutions, *Proc. Roy. Soc. (London)*, **99A** (1921), 196.

<sup>52</sup> MERICA, P. D., WALTENBERG, R. G. and SCOTT, H.: Heat-treatment of duralumin, U. S. Bur. Standards. *Sci. Paper* no. **347** (1919); *Trans. Am. Inst. Min. Met. Eng.*, **64** (1919), 41; *Chem. Met. Eng.*, **21** (1919), 551; KNERR, H. C.: Duralumin, *Trans. Am. Soc. Steel Treat.*, **3** (1922), 13.

<sup>53</sup> GAYLER, M. L. V.: The constitution and age-hardening of alloys of aluminum with copper, magnesium, and silicon in the solid state, *J. (Brit.) Inst. Met.*, **38** (1922), no. 2, 216; KONNO, S.: Investigation of duralumin, *Sci. Repts.*, *Tohoku Imperial Univ.*, **11** (1922), 269; FRAENKEL, W., and SCHENER, E., Researches on the duralumin problem, *Testing*, **1** (1924), 33.

precipitated. If, instead of cooling very slowly, the alloy (first heated at  $500^{\circ}\text{C}$ . long enough to insure homogeneity of the solid solution) is quenched, the solid solution can be retained as such, but in a metastable state. On standing for a week at room temperatures, spontaneous changes take place in the alloy and it becomes much harder, the hardness even doubling. Further change with time is very slight. A similar but more rapid change can be induced by heating, say to  $150^{\circ}\text{C}$ . for an hour. By such heat treatment, alloys of the duralumin type become very much stronger than the cast or wrought aluminum alloys that are not heat treated, and much more valuable for aircraft construction, for example. If the "maturing" temperature is raised to  $200^{\circ}\text{C}$ . and above, the hardness decreases.

The microscope does not reveal any alteration in the solid solution of the alloy immediately after quenching, or upon aging or maturing, until such temperatures are used in the reheating that the hardness and strength of the alloy are much decreased from the maximum. On such softened samples, however, it is found that  $\text{CuAl}_2$  and  $\text{Mg}_2\text{Si}$  begin to be visible and, on further softening, these constituents agglomerate.

This is explained by the assumption that, in aging or maturing, a precipitation of  $\text{CuAl}_2$  and  $\text{Mg}_2\text{Si}$  first occurs, but that the particles are, when first released from molecular solution, of such very small size as to be truly colloidal. These particles gradually coalesce, decreasing in numbers and increasing in size (though still below the resolving power of the microscope) till an optimum size and dispersion is reached which gives maximum hardness and resistance to slippage on the slip planes.

When the size of the particles becomes still larger and the number still less, the particles do not stiffen the alloy as much, and when they have grown to microscopic visibility, the alloy has been materially softened. Fortunately, the coalescence does not progress rapidly at room temperature and the alloy automatically ages to about the optimum size of particles and then action ceases, or, if the optimum dispersion is attained by accelerating the agglomeration to the proper degree by heating, the agglomeration is checked when the material is cooled to room temperature.

Jeffries and Archer<sup>54</sup> point out that if the particles project through the slip planes and key them against slippage, there will be a certain relationship between the size and number of these keys which will key the maximum number of planes. If there are more particles but they are too small, some planes will lack keys, while if there are too few larger particles, some planes will again lack keys.

This idea of the keying effect of a critical dispersion of a colloidal phase in process of agglomeration in a solid metal not only fits in with the facts in the case of duralumin, but at once applies to other alloys and indicates what was becoming plain from other evidence—that when we have a slanting line in an equilibrium diagram dividing a solid solution field from a two-phase field, with that solid solution as one phase, so that the solubility of the second phase in the solid solution decreases with fall of temperature, it may be possible, by suitable quenching and tempering, to control the agglomeration and dispersion of the second phase and thus regulate the physical properties within certain limits.

The phenomena met in heat treating steel can be similarly explained. The equilibrium diagram has no place for martensite, for troostite, or—without explanation that its constituents,  $\alpha$  iron (ferrite) and  $\text{Fe}_3\text{C}$  (cementite), are the same in composition as those formed from austenite on slow cooling—for sorbite. But these are distinct entities, both from microscopic appearance and from physical properties.

But it is now generally thought that when we rapidly quench austenite (solid solution, probably of carbon, perhaps of  $\text{Fe}_3\text{C}$ , in  $\gamma$  iron) the martensite which results is a solid colloidal suspension of carbon (or  $\text{Fe}_3\text{C}$ ) in iron (the iron being in either the  $\alpha$  or  $\beta$  form).

Troostite, which forms from martensite on heating, is now universally accepted as a colloidal suspension of  $\text{Fe}_3\text{C}$  in  $\alpha$  iron (with probably some free carbon present as well). On further heating, agglomeration of the  $\text{Fe}_3\text{C}$  takes place and sorbite appears.

<sup>54</sup> Slip interference theory of the hardening of metals, *Chem. Met. Eng.*, **24** (1921), 1057.

The hardness of martensite and the different degree of hardness of troostite agree well with the conception that martensite and troostite are solid colloidal suspensions,<sup>55</sup> in view of modern theories of hardness.

The varying properties of sorbite after reheating to different temperatures agree well with the idea of a varying degree of agglomeration of the cementite.

This question of the heat treatment of steel has been debated for a score of years, is very complicated, and is still highly controversial. To elaborate all the theories, even merely as they bear on the presence of colloidal phenomena, would require a book rather than part of a chapter. It is safe to say, however, that the ultimate theory for the hardening of steel must include the consideration of colloids.

The ideas of hardness, in solid solutions, as due to distortion of the space lattice by "stranger" atoms, and consequent changes of atomic forces between adjacent molecules; in fine crystals, as due to external interference with or stopping of movement on a slip plane due to presence of an adjacent, differently oriented crystal, so that less slip can occur in such material than in a coarse-grained one and the greater surface of the fine crystals or crystal fragments producing greater surface forces; and, in metastable mixtures, formed by decomposition of a solid solution, as due to the presence of a keying material of colloidal size, in colloidal dispersion, and the resulting softening with sufficient heating, as due to the agglomeration of the colloid beyond the critical dimensions, come close to giving a complete theory of, or set of theories of, hardening.

<sup>55</sup> DESCH, C. H.: Colloidal systems in solid crystalline media, Fourth Report on Colloid Chemistry and its General and Industrial Application, Brit. Assn. Adv. Sci. (1922), 33; LANTSBERRY, F. C. A. H.: Structure of steels from the standpoint of colloid chemistry, *J. Soc. Chem. Ind.*, **41** (1922), 409R; MEYER, H.: Colloidal chemistry and metallurgy, *Kolloid.-Z.*, **31** (1922), 310; SWINDEN, T.: A study of the constitution of carbon-molybdenum steels, *J. (Brit.) Iron Steel Inst.* (1913), no. 5, 100; VANICK, J. S. and SVESHNIKOFF, W. W.: Thermal transformations in some chromium-vanadium steels, *Trans. Am. Soc. Steel Treat.*, **3** (1923), 502; WESTGREN, N. and PHRAGMEN, G.: X-ray studies of the crystal structure of steel, *Engineering* (London), **113** (1922), 630; *J. Iron Steel Inst.*, Sept., 1922; BAEN, E. C.: The nature of martensite, *Trans. Am. Inst. Min. Met. Eng.*, no. 1299 S. Issued with *Min. Met.*, Feb., 1924.



In the slip interference theory, keying might be considered as due to surface forces of the particles of colloidal size acting on the adjacent slip planes almost as well as to the mechanical keying advanced by Jeffries and Archer, and when we consider that we are actually dealing with space lattices and atomic, molecular, and surface forces, instead of with a pile of cards with tacks through them as in the mechanical analog, the idea of surface forces as the hardening agent has much to commend it.

In whatever form these theories be utilized, it is plain that they depend on the presence of particles that are very small, whether or not they correspond to ordinary definitions of colloidal dimensions, and that the state of subdivision or agglomeration and the relative dispersion of the particles accounts plausibly for many observed facts.

Best of all, these theories are not in conflict with the equilibrium diagrams and with microscopic evidence, but they account for phenomena for which the phase rule and the microscope have no adequate explanation, but on which much of the commercial utility of metals and alloys depends.

Various other applications of phenomena due to material in a very fine state of subdivision might be cited in connection with metals and alloys, but the above examples will serve to indicate that the colloid chemist can offer the metallurgist ideas for explanation of puzzling facts and may in the future provide methods for improvement in metallurgical processes to which the colloid chemists viewpoint has not yet been applied.

When the colloid chemist realizes that his fundamental theories will be applied to metals and alloys at very high temperatures as well as to the ordinary materials and the range of temperatures with which he has so far chiefly dealt, and when he will experiment with metals and alloys in spite of the experimental difficulties, he will be more likely to develop theories which are universally accurate and applicable. The field of colloid chemistry applied to metals and alloys is almost untouched and offers much promise to the investigator.

The metallurgist of the future must pay attention to colloid chemistry, and it will at least do no harm to the colloid chemist if he will pay some attention to metallurgy.

## CHAPTER XXI

### COAL, COKE, AND TAR

By

ARNO C. FIELDNER, REINHARDT THIESSEN, AND JOSEPH  
D. DAVIS

#### ORIGIN OF COAL

**Formation of Peat.**—Peat<sup>1</sup> is composed of the altered remains of plant growth accumulated in bogs and swamps, under conditions favoring luxuriant growth and incomplete decay.

Dead plant substances rapidly undergo decay, initiated by fungi and maintained first by fungi, bacteria, and burrowing and boring insects, and, finally, by bacteria alone. The rate of decay and oxidation is greatest at the surface and rapidly diminishes at the horizon of submersion, becoming very slow or suspended after the plant substances are entirely submerged by the superincumbent debris added year by year.

Disintegration follows as the material becomes soft and brittle, yielding to the action of wind, rain, snow, and ice, and is greatest at the surface and is arrested more and more as it is covered up by later material. The result is a mass of debris of all possible stages of disintegration from large fragments of plant parts, such as stems, branches, barks, leaves, etc., down to a very fine pulp or attritus.

The various plant constituents and products have different resistances to oxidation and decay and do not contribute proportionately to the deposit. By far the largest bulk is furnished by the carbohydrates, and of these the celluloses contribute the major part. The sugars, starches, and gums are readily decomposed by

<sup>1</sup> WHITE, D. and THIESSEN, R.: Bureau of Mines *Bull.* **38** (1914) (a chapter on the formation of peat by C. A. Davis).

DACHNOWSKI, A.: "Peat Deposits of Ohio," Geol. Survey of Ohio *Bull.* **16** (1912).

living organisms, as are also the hemicelluloses, pentosans, the hexoses, and the pectins of the cell-wall carbohydrates. The celluloses are more resistant, and the suberized and cutinized cell walls are the most resistant.

Wood or lignocellulose constitutes the bulk of most plants. It is composed essentially of cellulose and a lignone complex in about equal proportions. Celluloses decompose more easily than the lignone complex. In decaying wood, the lignone content remains nearly constant, while the cellulose content decreases rapidly. Agencies of decay change lignocellulose into so-called "humins," consisting partly of water-soluble and partly alkali-soluble substances, and an insoluble residue much richer in carbon.

Not only carbohydrates but glucosides, tannins, essential oils, resins, terpenes, camphors, and vegetable bases contribute materially to the deposits. Most of these compounds are not so easily decomposed. The amount a substance finally contributes to the deposit may not be proportional to the amount present in the plant originally, owing to varying resistance to decay and putrefaction.

**Colloidal Nature of Peat and Humin.**—Peat and humus substances behave as colloids, in that they show the Tyndall effect, adsorptive power, undergo cataphoresis, tan leather, and act as protective colloids.<sup>2</sup> There are all degrees of dispersion in the bog, varying from hydrosol to hydrogel. Much of the peat substance is in its original plant structural form, but with the cell walls forming the tissues in a hydrogel condition. Occasionally, small sections of peat deposits are found in which cell structure has entirely disappeared. Such jelly-like masses are called *dopplerite*.

Peat readily adsorbs alkalies, acids, salts—electrolytes in particular—dyes and gases, starch, and iron hydroxide in varying amounts, depending on the condition of the peat and the substances to be adsorbed.<sup>3</sup>

<sup>2</sup> VAN BEMMELEN: *Landw. Vers.-Sta.*, **35** (1888), 69; EHRENBERG: *Chem. Ztg.*, **34** (1910), 1157; BAUMAN and GULLY: *Mitt. kgl. Bayer Moorkultur-anstalt*, **3** and **4** (1911).

<sup>3</sup> ROHLAND: *Kolloid-Z.*, **16** (1915), 146; OSTWALD and WOLSKI: *Ibid.*, **30** (1922), 119; OSTWALD: *Ibid.*, **29** (1921), 316.

Peat as dug contains from 50 to 90 per cent water. The greater part of this water is colloiddally retained as the dispersing medium of the peat hydrogel in which the original plant structure is usually preserved in considerable detail. Peat gels may contain over 90 per cent of water and yet retain their shape and be cut with a knife in the same way that agar and fruit jellies may be cut. The application of high pressures on unmacerated peat removes but little more than the occluded water.<sup>4</sup> Peat gels may be coagulated by heating, freezing, electrolysis, and the addition of electrolytes. The freezing and thawing of peat have both a peptizing and a coagulating effect. Most of the commercial processes proposed for dewatering peat depend on air-drying after freezing and thawing, or heating the raw macerated peat with hot flue gases or steam.<sup>5</sup>

**Formation of Coal.**—It has already been shown how coal-forming material was laid down in beds analogous to the peat deposits of today, in undrained basins similar to the Dismal Swamp of Virginia, the Everglades of Florida, and the peat bogs of Minnesota, Wisconsin, and Michigan, but on a much larger scale. Meanwhile, the level of these areas were slowly subsiding, the plant growth keeping pace with the subsidence for a long period of time, until eventually the depth of water became too great for plant growth to continue, and the deposit became covered with silt which formed the roof shales of the present-day coal beds. The peat hydrogel of the biochemical stage of coal formation was gradually compressed by the superincumbent load of sediments and, finally, deprived of much of its water. It hardened as a natural consequence of its hydrogel state. Pressure caused by the superincumbent rock, augmented by earth thrusts, and perhaps temperatures, not necessarily high, were factors in the coalification processes.<sup>6</sup>

#### THE CONSTITUTION OF COAL

As shown in Fig. 1, bituminous coals are of a highly laminated structure and are compiled of various layers differing from

<sup>4</sup> HAUSDING: "Handbuch Torfgewinning," Parey, Berlin, 1921.

<sup>5</sup> OSTWALD: *Kolloid-Z.*, **29** (1921), 316; **30** (1922), 119; KEPPELER: *Brennstoff-Chem.*, **3** (1922), 249, 262.

<sup>6</sup> WHITE and THIESSEN: U. S. Bureau of Mines *Bull.* **38** (1914).



one another in luster, texture, and fracture, and varying greatly in thickness. In general, two alternating kinds of layers stand out in sharp contrast. The one is glossy jet-black, free from striations, and the other is dull grayish-black and striated. The former, usually called "bright coal," is compact and breaks with a definite conchoidal fracture; and the latter called "dull coal," is less compact and tends to fracture along the horizontal laminated structure. The bright coal is embedded in the dull coal in

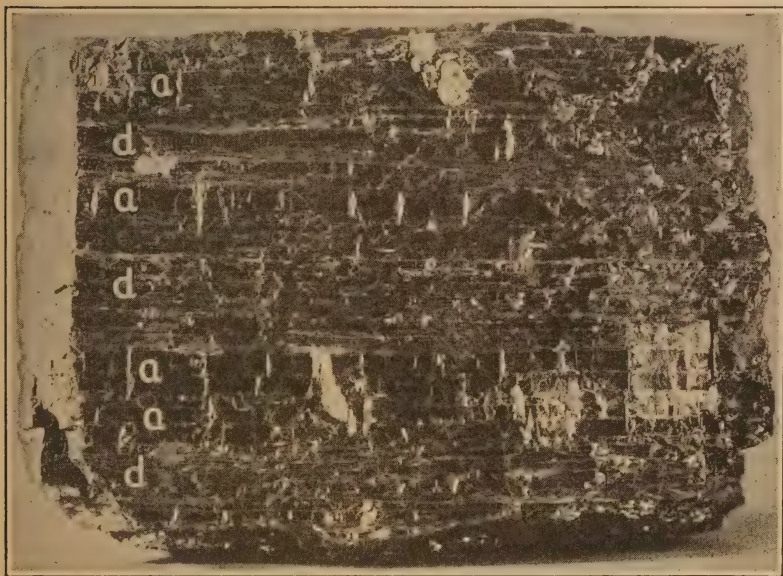


FIG. 1.—Lump of Illinois coal. *a*, Bands of anthraxylon; *d*, dull coal. (Three-quarters natural size.)

lenticular masses. The dull coal is further sublaminated with very thin laminæ of bright coal embedded in the ground mass of dull coal.

**Composition of the Coal.**—Microscopic examination of thin sections of bright coal shows it to be derived from the woody parts of plants. Thiessen<sup>7</sup> has given the name of *anthraxylon*, meaning coal from wood, to the bright coal. (See Fig. 2.) It consists of the coalified trunks, branches, and twigs of trees and chips of wood of the peat.

<sup>7</sup> U. S. Bureau of Mines *Bull.* 117 (1920).

Microscopic examination at low magnification of a polished vertical section of dull coal shows that it is composed of thin layers or lenses of bright coal embedded in a ground mass of dull coal. These thin layers of bright coal are of the same composition and origin as the thicker layers which are visible to the naked eye. They simply come from smaller fragments of wood. The

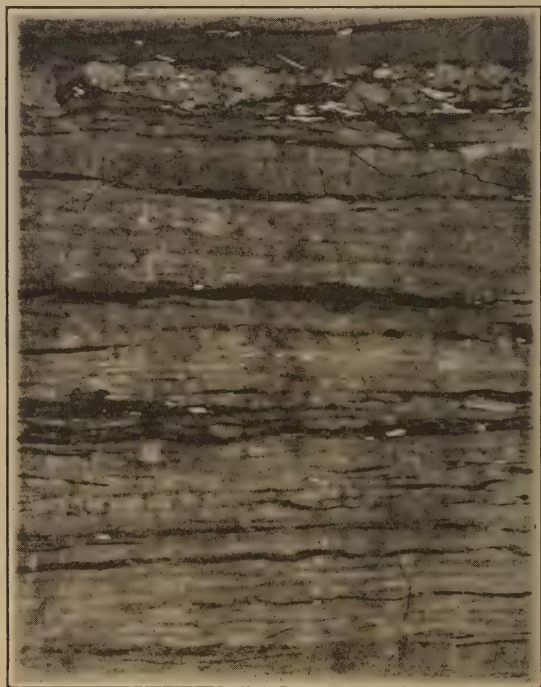


FIG. 2.—Vertical thin section of Pittsburgh coal. Bright coal compiled of thin bands of anthraxylon. (150 diameters.)

ground mass of dull coal, termed *attritus* by Thiessen, consists of the highly macerated plant remains which have been previously described under the formation of peat. (See Fig. 3.) Examination of thin sections under high magnification shows recognizable remains of leaves, bark, cuticle, cortex, spore exines, pollen exines, bits of plant tissue, intermixed with resinous, carbonaceous, and mineral matter.

Spore exines (see Figs. 4 and 5), owing to their golden-yellow color and translucency, are the most conspicuous constituents of the attritus. The spore exines are the resistant wax and oil-impregnated coatings of the spores of Paleozoic *pteridopfytes*. They are found in various forms, sizes, thicknesses, and sculpturing.



FIG. 3.—Vertical thin section of Pittsburgh coal. Dull coal, showing attritus rich in spore matter with several thin bands of anthraxylon. (150 diameters.)

Coal contains mineral matter which forms the ash left on burning, and this varies greatly in amount, fusibility, and chemical composition.<sup>8</sup> The mineral matter of coal may be differentiated into three classes: (1) bands, partings, and nodules of clay, silica, pyrite, calcite, and gypsum; (2) fine microscopic

<sup>8</sup> FIELDNER, HALL and FEILD: U. S. Bureau of Mines *Bull.* **129** (1918) (contains a complete bibliography); SELVIG and FIELDNER: *Ibid.*, **209** (1922).



particles or thin sheets; (3) colloidal matter uniformly dispersed, ultramicroscopic and not removable by coal-washing methods.

All coals contain inorganic sulfur as pyrite ( $\text{FeS}_2$ ) and frequently some as sulfate, the pyrite occurring as nodules and lenses and as microscopic particles<sup>9</sup> disseminated in the coal. Coal also con-

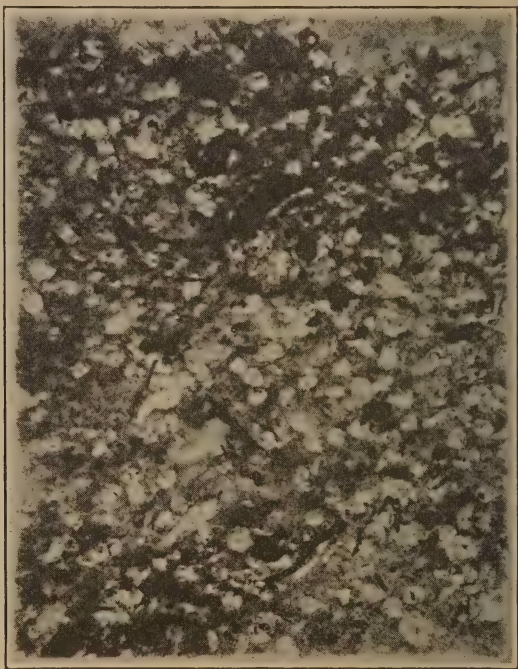


FIG. 4.—Horizontal thin section of Pittsburgh coal. Showing attritus rich in spore matter. (150 diameters.)

tains organic sulfur compounds of unknown structure, which Powell and Parr<sup>10</sup> differentiate into *resinic* and *humic* compounds, the former being a constituent of that portion soluble in phenol. The relative proportions of organic and pyritic sulfur in different coals vary and either form may be in excess.<sup>11</sup> It is probable that

<sup>9</sup> THIESSEN: *Trans. Am. Inst. Mining Met. Eng.*, **63** (1919–20), 913.

<sup>10</sup> POWELL and PARR: *Univ. Ill. Eng. Exp. Sta. Bull.* **111** (1919); POWELL: *Proc. Eng. Soc. Western Penn.*, **36** (1920), 611; U. S. Bureau of Mines *Tech. Paper* **254** (1921).

<sup>11</sup> YANCEY and FRASER: *Univ. Ill. Eng. Exp. Sta. Bull.* **125** (1921).



the massive pyrite was deposited in the coal from sulfur and iron-bearing waters, but the finely disseminated pyrite and organic sulfur may have a common origin in the coal-forming plants.<sup>12</sup>

**Colloidal Nature of Coal.**—A study of the origin and formation of coal shows that by far the largest proportion of the contributing substances were of the nature of colloids and remained so through the various stages of the coalification processes. The

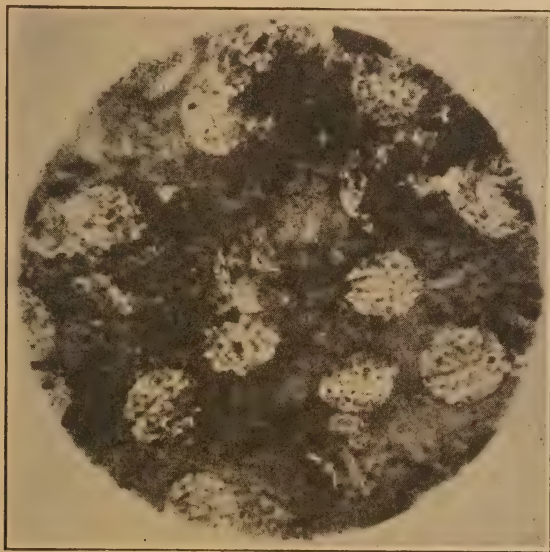


FIG. 5.—Part of section shown in Fig. 4 more highly magnified to show constituents in detail. (750 diameters.)

colloidal properties of coal are evident from microscopic examination and from its physical and chemical characteristics. Humins and the humic portions of peat are dispersed as hydrosols by alkalies. This same peptization occurs, although to a less degree, when lignites and thoroughly weathered bituminous coals are treated with alkaline solutions. True bituminous coal and anthracite show little if any peptization under these conditions. In general, the peptizing effect decreases with decrease in the per-

<sup>12</sup> THIESSEN: *Trans. Am. Inst. Mining Met. Eng.*, **63** (1919-20), 913.

centage of volatile matter and is much greater in lignite than in bituminous coal.<sup>13</sup>

When lignites and bituminous coals are digested with a solution of from 15 to 30 per cent of nitric acid and a saturated solution of potassium chlorate for a sufficient length of time, and then treated, after being washed with water, with an alkali (preferably ammonium hydroxide), they will dissolve almost completely, forming colloidal solutions. Anthracite, boghead, and cannel coals react but slightly or not at all.

### THE PHYSICO-CHEMICAL BEHAVIOR OF COAL

Investigators interested in the constitution of coal have long sought to separate the constituents of coal by treatment and extraction with various organic solvents, such as benzol, ether, pyridine, aniline, quinoline, picoline, phenol, etc. No coal or lignite dissolves completely in any of these solvents. Owing to the readiness with which the extracted materials of coal oxidize and polymerize, it is extremely difficult, if not impossible, to follow through such separations to definite identifiable chemical compounds with any degree of certainty that these end compounds existed as such in the coal. Nevertheless, extraction with inert solvents is probably our best method of isolating some of the chemical compounds existing in coal, in the least changed if not in an unchanged condition.

**Extraction of Coal with Organic Solvents.**<sup>14</sup>—Bedson<sup>15</sup> subjected pulverized coal to the action of pyridine in Soxhlet extraction apparatus for several hours until the effluent became colorless. The "solutions" so obtained were dark brown in color and sometimes showed a green fluorescence. The dissolved matter was either precipitated with dilute hydrochloric acid, filtered off, washed, and weighed, or the pyridine extract was evaporated to

<sup>13</sup> BOUDOUARD: *Compt. rend.*, **147** (1908), 86; **148** (1909), 284; HOFFMANN: *Repts. Progr. Geol. Survey, Canada*, Pt. M (1885), 1-44; DONATH and DITZ: *Oesterr. Z. Berg-Hüttenw.*, **51** (1903), 310; BARSCH: *Jahrb. kgl. Preuss. geol. Landesanst.* (1908).

<sup>14</sup> BAKER: *J. Soc. Chem. Ind.*, **20** (1901), 789; *Trans. N. Eng. Inst. Mining Mech. Eng.*, **50** (1901), 23.

<sup>15</sup> *Ibid.*, **48** (1899), 82; *J. Soc. Chem. Ind.*, **27** (1908), 147.

dryness in an air current, the dried residue then broken up and heated on a water bath until the odor of pyridine disappeared, and then weighed. The yield of pyridine extract varied from practically zero with anthracite to 35 and 40 per cent in good gas coals. The residue from the extraction had but little coking property. Since Bedson's work with pyridine, a number of other investigators have attempted to separate or classify some of the constituents of coal by this method or some modification of it.<sup>16</sup> The results of these workers show that the highest extract is obtained with bituminous coal, although not in the same proportion as the volatile matter of the coal. Anthracite, semi-anthracite, and "mother of coal," or mineral charcoal, show little or no extract; brown coals, cannel, and boghead coals yield relatively low percentages of extract.

The action of pyridine on coal and the nature of the "solution" are not definitely known. Bone<sup>17</sup> states that "besides any ordinary solvent action which pyridine may have upon the resinic constituents, which is probably fairly rapid, it also at the same time slowly attacks and resolves into simpler molecular aggregates the complex structure of the coal substance as a whole." Contrary to Bone, Harger, Glud, Lewes, Fischer, and Illingsworth, Hoffmann and Damm consider it a true solution. There is no work on record to show whether the solution obtained by the action of pyridine on coal is a true molecular or colloidal solution. Addition of acids to the pyridine extract of coal produces an amorphous chocolate-brown precipitate insoluble in water and alcohol, and partly soluble in certain organic solvents, as chloroform and benzol. It is easily oxidized by nitric acid.

<sup>16</sup> WHEELER and BURGESS: *J. Chem. Soc.*, **99** (1911), Pt. II, 649; WHEELER and CLARK: *Ibid.*, **103** (1913), Pt. III, 1704; WHEELER and JONES: *Ibid.*, **105** (1914), 2562; **107** (1915), 1318; BONE and SARGENT: *Proc. Roy. Soc. (London) A.*, **96** (1920), 119; BONE: "Coal and its Scientific Uses," Longmanns Green Co., London, 1919; BONE, PEARSON, SINKINSON and STOCKINGS: *Proc. Roy. Soc. (London) A.*, **100** (1922), 582; ILLINGSWORTH: *Fuel*, **1** (1922), 3, 17, 50, 65, 89; **1** (1922), 213; *Proc. S. Wales Inst. Eng.*, **38** (1922) 499; TIDESWELL: *Fuel*, **1** (1920), 244; HARGER: *J. Soc. Chem. Ind.*, **33** (1914), 389; DENNSTEDT and BÜNZ: *Z. angew. Chem.*, **21** (1914), 1825. HOFFMANN and DAMM: *Mitt. Schlesischen Kohlenforschungsinstit., Kaiser Wilhelm-Gesell.*, **1** (1922), 115; FISCHER and GLUD: *Gesam. Abhand. Kennt; Kohle*, **1** (1915-16), 54; GLUD: *Ibid.*, **1** (1915-16), 43.

<sup>17</sup> *Loc. cit.*, p. 93.

Stopes and Wheeler<sup>18</sup> have designated the three groups obtained by the action of solvents on coal as follows:

$\alpha$  compounds—insoluble in pyridine.

$\beta$  compounds—soluble in pyridine and insoluble in chloroform.

$\gamma$  compounds—soluble in pyridine and chloroform.

They define these three products as follows:

The  $\alpha$  product is a brown powder. It does not fuse, and yields very small percentages of tars, which consist almost entirely of phenols.

The  $\beta$  product is a brown powder, and is only distinguishable from the  $\alpha$  product by its solubility in pyridine.

The  $\gamma$  product has the appearance of a resin or lac and melts at 100°C.

Wheeler and his associates conclude that the  $\alpha$  and  $\beta$  products are derived almost entirely from cellulose, while the  $\gamma$  product is derived from the resinous constituents of coal, the original source of which is resins, sugars, starch, and rubbers.

On the other hand, Fischer and Schrader<sup>19</sup> argue that the cellulose has disappeared entirely during the first coal-forming stage and that the degradation products of the lignone complex alone have survived to contribute to the coal, the cellulose having been decomposed to methane, carbon dioxide, and water.

Many other organic solvents have been tried for the extraction of coal with more or less success. The bases aniline and quinoline were found by Vignon<sup>20</sup> to have a solvent action similar to, but greater than, that of pyridine. Parr and Hadley<sup>21</sup> dissolved from 20 to 40 per cent of Illinois coal with phenol, and Fischer and Gluud<sup>22</sup> extracted 6.7 per cent of a coal with benzene at a temperature of 275°C. Alcohol and ether have been used as extractive agents by many investigators, but they have the disadvantage that they dissolve very little of the coal substance.

In general, the higher boiling solvents, particularly the bases, have the strongest solvent action on coal; none of the low boil-

<sup>18</sup> Monograph on Constitution of Coal, Dept. of Sci. Ind. Research London, 1918.

<sup>19</sup> *Brennstoff-Chem.*, **3** (1922), 65.

<sup>20</sup> *Compt. rend.*, **158** (1914), 1421.

<sup>21</sup> *Univ. Ill. Exp. Sta. Bull.* **76** (1914).

<sup>22</sup> *Ges. Abhandl. Kenntnis Kohle*, **1** (1917), 54.



ing solvents have any pronounced action, even under pressure and near their critical temperatures.

**Adsorption of Gases by Coal.**—That coal adsorbs gases has been demonstrated by many workers.<sup>23</sup>

Under the adsorption of gases by coal, the adsorption of oxygen is of the greatest interest and significance, as it is involved in the weathering and spontaneous combustion of coal.

When fresh coal in the bed is exposed to air, two active processes are set up immediately—an evolution of hydrocarbons, mainly methane, and an adsorption of oxygen. The exchange of gases proceeds simultaneously but independently of each other. The methane is evolved rapidly at first, but decreases in rate to very small quantities at the end of two months.<sup>24</sup>

The avidity for oxygen is of longer duration, there being measurable adsorption of oxygen over a period of years. It is not definitely determined whether the oxygen combines chemically with the coal or is adsorbed only in the coal substance. Oxygen so retained that it cannot be recovered from coal by the vacuum pump is considered by Graham<sup>25</sup> to be chemically combined. Coal certainly takes up some oxygen by adsorption. It is possible that this surface-adsorbed oxygen then combines with the coal, being released at higher temperatures and under vacuum as CO and CO<sub>2</sub>. Richter<sup>26</sup> agrees that the initial process is strictly physical but is followed by chemical reaction. Fine coal dust oxidizes more rapidly than coarse coal and the oxidizable material contained in it is used up at a rate correspondingly rapid.

<sup>23</sup> RICHTERS: *Dinglers Polytech. J.*, **195** (1870), 315; MAHLER: *Ann. mines*, **4** (1913), ser. 11, 163; *Colliery Guardian*, **106** (1913), 891; PARR and BARKER: *Univ. Ill. Eng. Exp. Sta. Bull.* **32** (1909); PORTER and OVITZ: *U. S. Bureau of Mines Tech. Paper* **2** (1911); THIESSEN: *U. S. Bureau of Mines Bull.* **82** (1912); LE PRINCE RINGUET: *Compt. rend.*, **158** (1914), 573; WINMILL: *Trans. Inst. Mining Eng.*, **46** (1913–14), 563, 578; **48** (1914–15), 503, 514; **51** (1915–16), 493; *Colliery Guardian*, **108** (1914), 564; GRAHAM: *Trans. Inst. Mining Eng.*, **48** (1914–15), 521; **49** (1914–15), 35; **52** (1916–17), 348; PORTER: *U. S. Bureau of Mines Tech. Paper* **65** (1914); KATZ: *Ibid.*, **147** (1917).

<sup>24</sup> WINMILL: *Trans. Inst. Mining Eng.*, **46** (1913–14), 563.

<sup>25</sup> *Trans. Inst. Mining Eng.*, **52** (1916–17), 338.

<sup>26</sup> *Dinglers Polytech. J.*, **195** (1870), 315.

Lamplough and Hill<sup>27</sup> measured the heat evolved per cubic centimeter of oxygen absorbed for a number of English coals. The values ranged from 2.8 to 3.7 cal., and averaged 3.3 cal. Winmill<sup>28</sup> obtained 2.1 cal. per cubic centimeter of oxygen adsorbed, and discovered an error in Lamplough and Hill's work which, after correction, brought their figures into agreement with his own.

**Moisture in Coal.**—Freshly mined coal always contains moisture, the amount depending upon the rank or grade of the coal. In general, the amounts decrease directly in going from the lower ranks to the higher ranks. Much of it is lost, more or less rapidly, according to the nature and fineness of the coal and the humidity and temperature of the atmosphere to which it is exposed. A coal which has undergone a considerable amount of air-drying when the air is dry is liable to absorb moisture during wet periods. The retentivity or quality of holding moisture is due to its colloidal nature.

Mack and Hulett<sup>29</sup> calculated that if a cubic centimeter of coal, moisture- and ash-free, were divided into little cubes  $10^{-6}$  cm. or  $0.01\mu$  on each edge, the total surface of these cubes would be 600 sq. m., and if each particle were covered with water  $10^{-8}$  cm. or  $0.1\mu\mu$  thick with a density of one, there would be 0.06 cc. of water on these faces, or 6 per cent of the mass. This water would have no vapor pressure. If the thickness of the film were increased to one-tenth of the cube, or 10 molecules thick, there would be 0.6 cc., or 60 per cent, of water of the mass associated with the original cubic centimeter of coal. The vapor pressure would be much below that of water in bulk at the same temperature.

**Coal Washing by Froth Flotation.**—When air is beaten into a mixture of finely ground coal, water, and a small amount of oil, bubbles are formed which carry the carbonaceous material in a froth to the surface, while the mineral matter remains suspended in the water.<sup>30</sup> This process, known as froth flotation, depends for its operation on the relative magnitude of the interfacial

<sup>27</sup> *Trans. Inst. Mining Eng.*, **45** (1912-13), 629.

<sup>28</sup> *Trans. Inst. Mining Eng.*, **48** (1914-15), 508.

<sup>29</sup> *Am. J. Sci.*, **43** (1917), 89.

<sup>30</sup> RALSTON: *Chem. Met. Eng.*, **26** (1922), 500.

tensions between water, oil, air, coal, and mineral matter. Oil tends to displace water on the carbonaceous particles, while water will displace oil on the particles of mineral matter. When air is beaten into the mixture, a liquid film of oil and water is formed around each bubble, the surface tension of which is less and the viscosity greater than the bulk of the liquid. The particles of coal, being more readily wet by oil than by water, attach themselves to the oily bubble film and these "armor-plated" bubbles rise to the top in a stable froth, leaving the mineral matter in the water.

Of the various types of machines in use in the metallurgical field, the M. S. Standard,<sup>31</sup> in which air is beaten into the mixture, and the Ruth machine,<sup>32</sup> of the subaerated type, have been found adaptable to coal washing. The amount of frothing oil used is relatively small. Ralston reports a series of tests in which the oil used varied in amount from 0.42 to 1.11 lb. per ton of coal. A mixture of 6 parts alphanaphthylamine with 4 parts xylidine gave the best results; pine tar and the coal tar products were not suitable. With coals not containing boney coal or carbonaceous shale, ash reduction and combustible recovery are high; bone coal and carbonaceous shale tend to come over in the concentrate or must be discarded as a "middling product" with a consequent low combustible recovery.

**The Trent Process of Cleaning Coal.**—The Trent process of cleaning coal<sup>33</sup> consists in mixing finely pulverized coal with water and agitating with oil in an amount equal to 25 to 30 per cent of the coal. The carbonaceous material forms with the oil a pasty agglomerate or *amalgam*, which is heavier than water, while the mineral matter, which was physically separated from the carbonaceous material by the fine pulverization, remains suspended and can be drawn off with the water.

The process depends upon the same principles of selective wetting which have made froth flotation possible. When oil is stirred into a suspension of coal in water, the first tendency is

<sup>31</sup> BURY, BROADBRIDGE and HUTCHINSON: *Trans. Inst. Mining Eng.*, **60** (1920-21), 243.

<sup>32</sup> RALSTON and YAMADA: *Chem. Met. Eng.*, **26** (1922), 1081.

<sup>33</sup> PERROTT and KINNEY: *Chem. Met. Eng.*, **25** (1921), 182; BATLEY: *Fuel*, **2** (1923), 236; DAVIS and COLEMAN: *Chem. Met. Eng.*, **26** (1922), 173.

probably the formation of a suspension of droplets of oil in the mixture. The coal particles are, however, so readily wet by oil in preference to water that the globules rapidly become small agglomerates of coal and oil. These agglomerates tend to adhere to one another and as a result of further agitation coalescence reaches a point where a large amount of entrapped water is released from between the particles and a more or less homogeneous mass of clean coal and oil is formed. The mineral matter, being more readily wet by water than by oil, remains suspended in the water.

Work done by the Bureau of Mines on this problem has led to conclusions as follows:

1. Separation of mineral matter from coal is not complete, since much of the mineral matter is so intimately associated with the coal that it cannot be separated by pulverization. Certain sub-bituminous coals and lignites are not amenable to treatment by the process because of the finely disseminated condition of the mineral matter.

2. Any oil, the viscosity of which is not too great, may be employed, but coal tar and other oils tending to form emulsions with water result in a product containing a higher amount of ash than is obtained by use of the paraffin oils.

3. Ash reduction varies from 35 to 70 per cent, depending on the character of the coal; combustible recovery is usually high, ranging from 95 to 99 per cent. The sulfur content of the coal is not materially reduced.

**Colloid Fuels.**—Colloidal fuels are discussed by Sheppard, in Chap. XXII of this volume, and, therefore, will be omitted from consideration at this place.

#### THE FORMATION AND STRUCTURE OF COKE

Bancroft<sup>34</sup> states: "The formation of coke involves the obtaining of a granular structure giving strength and porosity. A knowledge of colloids is essential to anyone who really wishes to understand about coke."

Beilby<sup>35</sup> believes that the carbon compounds in coke are in

<sup>34</sup> *Chem. Met. Eng.*, **23** (1920), 454.

<sup>35</sup> *Fuel*, **1** (1922), 225.



a vitreous state, apparently basing his conclusions on the glassy appearance of the thin cell walls under the microscope.

Certain constituents of the coke may form supercooled solutions, but the largest part of coke is granular and a heterogeneous mixture of various residues cemented together in a porous structure. The determination and identification of this cementing material in coal have constituted the goal of many investigators.

Fischer and Gluud<sup>36</sup> term those coal constituents which melt, *bitumens*. The bitumens include the constituents extracted by benzol, under pressure, and on their properties depends the coking power of the coal. In good coking coals the bitumens melt at about 300 to 350°C., and gradually decompose in part, giving off gases, the residual portion continually rising in melting point and eventually hardening into a firm, dense coke. The porous, weak coke, produced by high volatile gas coals, is attributed to the distillation of a large part of the bitumens from the coal as undecomposed volatile matter. The non-coking of lean coals is due to the decomposition of the bitumens in the coal before they have been heated to their melting temperatures.

Illingsworth<sup>37</sup> ascribes the degree of plasticity of fusing coal to the amount of "resinic" matter ( $\gamma$  components, soluble in pyridine and chloroform), and the melting point and viscosity of the melted resinic constituents. The physical properties of the resulting coke are determined largely by the temperature to which the coal is subjected in the coking process and the proximity of that temperature to the melting and decomposition temperature of the resinic constituents. He showed experimentally that approximately 400° was the coke-forming temperature of coals producing porous coke; and from 430 to 450° for coals producing dense coke; and that, in the carbonization of intimate mixtures of any two of the three coal components,  $\alpha$ ,  $\beta$ , and  $\gamma$ , at temperatures varying from 450 to 900°, only those mixtures containing "resinic" ( $\gamma$ ) substances were capable of giving a residue of a coherent nature. Consequently, solely to the "resinic" ( $\gamma$ ) portions of a coal must be ascribed the property of causing the cohesion of a coal into a coke when carbonization takes place. He believes that the "resinic" bodies melt at 200°, and become

<sup>36</sup> *Ges. Abhandl. Kenntnis Kohle*, **3** (1918), 35.

<sup>37</sup> *Colliery Guardian*, **119** (1920), 1441.

fluid at 350°. The plasticity of the coal is attributed to the liquidation of the resins with heat, and the subsequent flow of the fluid or semi-fluid resinic matter around the solid ingredients of the coal.

Fischer and Illingsworth both attribute the coking property of coal to certain easily fusible constituents that may be extracted with organic solvents. Similar views were held by earlier workers in this field.<sup>38</sup> Bone,<sup>39</sup> however, believes "that the 'resinic' constituents of coal play a relatively subordinate rôle in determining its coking properties"; and Charpy and Godehot<sup>40</sup> state that the coking properties of coal are largely dependent on certain constituents of cellulosic origin which, under the influence of heat, react with the tar and pitch, cementing the mass into coke.

It is evident that our knowledge of the constitution of coal is yet too fragmentary completely to understand the mechanism of coke formation, and it is hoped that colloid chemists will turn their attention to this problem.

**Water in Coke.**—The cell space of coke is usually between 40 and 60 per cent. The use of too much water in quenching causes a part of this cell space to become filled with water. It is possible to add as much as 28 to 35 per cent in this manner,<sup>41</sup> but, with careful quenching, the water content need not exceed 1 or 2 per cent. Unlike coal, dried coke is practically non-hygroscopic; Selvig and Kaplan<sup>42</sup> exposed powdered coke in atmospheres of various humidities and found that the moisture content in equilibrium with air at 50 per cent humidity ranged from 0.4 to 1.8 per cent in four different varieties of coke. Furthermore, coke does not retain residual moisture after drying at 105°; Fieldner and Selvig<sup>43</sup> have shown experimentally that the temperature and humidity of the drying atmosphere may be varied over a considerable range without influencing the result to any material

<sup>38</sup> DONATH: *Stahl u. Eisen*, **34** (1914), 60; PARR: 8th Int. Cong. of App. Chem., **10** (1912), 251; LEWES: *J. Roy. Soc. Arts*, **60** (1911), 135.

<sup>39</sup> *Combustion*, **3** (1920), 26.

<sup>40</sup> *Compt. rend.*, **164** (1917), 906.

<sup>41</sup> JOHANNSEN: *Stahl u. Eisen*, **28** (1908), 997.

<sup>42</sup> *J. Ind. Eng. Chem.*, **12** (1920), 783.

<sup>43</sup> U. S. Bureau of Mines *Tech. Paper* **148** (1917).

degree. Estimation of the true moisture content of coke presents none of the difficulties peculiar to coal and colloidal substances.

**Adsorption of Gases by Coke.**—Ordinary coke has practically no adsorptive capacity for gases and vapors in the sense that charcoal or even coal possesses that property. Chaney and St. John<sup>44</sup> show that an inactive form of carbon is deposited by the decomposition of hydrocarbons at high temperatures. Coal when carbonized at sufficiently low temperatures (below 600°) produces a coke which can be activated by selective oxidation with steam or air so that it will adsorb large quantities of gases and vapors.

**The Combustibility of Coke.**—The combustibility of coke is the rate of progression of the combustion under a defined set of conditions;<sup>45</sup> it is a function of those properties of the coke itself which affect the rate at which the reaction of coke carbon with oxygen, carbon dioxide, or water vapor proceeds.

Perrott and Fieldner,<sup>46</sup> Fischer, Breur, and Broche,<sup>47</sup> and others have measured the combustibility of cokes when heated in a constant stream of CO<sub>2</sub> under strictly similar conditions in a laboratory apparatus at various temperatures ranging from 600° to 1,100°C. Bähr<sup>48</sup> and many earlier investigators have made similar laboratory tests in oxygen or air.

Sherman and Blizard,<sup>49</sup> using the Kreisinger experimental furnace, determined the relative combustibility of four widely different kinds of blast-furnace cokes by taking gas samples at various points in the fuel bed and calculating, from analyses of these, the percentage completeness of combustion attained at the point of sampling, according to the following formula:

$$\text{Percentage completeness of combustion} = \frac{\text{CO}_2 - \text{CO}}{2\text{CO}_2 + \text{CO} + 2\text{O}_2} \times 100.$$

The total range of the completeness of combustion at the top of a 12-in. fuel bed was from 73 to 77 per cent when the coke was

<sup>44</sup> *Ind. Eng. Chem.*, **15** (1923), 1244.

<sup>45</sup> BRASSET in Johnston's "Principles, Operation and Products of the Blast Furnace," McGraw-Hill Book Co., 1918.

<sup>46</sup> *Proc. Am. Soc. Test. Materials*, **23** (1923), Pt. II, 475.

<sup>47</sup> *Brennstoff-Chem.*, **4** (1923), 33.

<sup>48</sup> *Brennstoff-Chem.*, **4** (1923), 312.

<sup>49</sup> *Trans. Am. Inst. Mining Met. Eng.*, **69** (1923), 526.

burned at a rate of approximately 25 lb. per square foot of grate area, per hour. These differences are relatively small and not enough to correlate the structure and other physical properties of the coke with its suitability for metallurgical use. The size of the coke did have a pronounced relation to the combustibility. The greater surface of coke, provided by an equal volume of smaller pieces, markedly increased the completeness of combustion at a given point in the fuel bed.

It is generally assumed that the combustibility of coke is governed by its size, the chemical and physical composition of the carbonaceous substance forming the cell walls, and the interior and surface structure of the coke pieces.<sup>50</sup>

Heyd<sup>51</sup> represents the views of a smaller group who recognize the importance of structure and chemical composition of the coke substance but think that the inorganic constituents and the manner in which silica and other ash-forming materials are dispersed in the coke are the principal factors governing combustibility. Unfortunately the experimental evidence supporting these views is very meager. The experiments of Baer<sup>52</sup> in oxygen and of Perrott and Fieldner<sup>53</sup> in CO<sub>2</sub> showed no perceptible relation between combustibility and porosity. Neither has anyone proved a relation between apparent density, strength or hardness of coke, and combustibility. It is probable that the ultramicroscopic structure, rather than the macroscopic structure, affects combustibility. Fischer<sup>54</sup> found that low-temperature coke, free from carbon deposited by the cracking of primary tars, reacted more rapidly with CO<sub>2</sub> than high-temperature coke. This greater combustibility was not due to the higher volatile matter content of low-temperature coke, since low-temperature cokes which had been heated in a neutral atmosphere at 1,100°C. showed the same combustibility as before heating.

<sup>50</sup> BRASSERT in Johnston's "Principles, Operation and Products of the Blast Furnace," McGraw-Hill Book Co., 1918; FISCHER, BREUR and BROCHE: *Brennstoff-Chem.*, **4** (1923), 33; SUTCLIFF and EVANS: *J. Soc. Chem. Ind.*, **41** (1922), 196; SCHREIBER: *Brennstoff-Chem.*, **4** (1923), 273.

<sup>51</sup> *Ibid.*, **4** (1923), 198.

<sup>52</sup> *Brennstoff-Chem.*, **4** (1923), 312.

<sup>53</sup> *Proc. Am. Soc. Test. Materials*, **23** (1923), Pt. II, 475.

<sup>54</sup> *Brennstoff-Chem.*, **4** (1923), 33.



Schreiber<sup>55</sup> and Baer<sup>56</sup> found that severe cracking of distillation products greatly decreased the combustibility of the resulting coke in oxygen and in air; and Chaney<sup>57</sup> found that carbon formed by the high-temperature decomposition of hydrocarbons was resistant to oxidation by steam and could not be activated for gas-adsorbing purposes.

Baer<sup>58</sup> believes that iron oxide in coke increases its combustibility catalytically. His belief is based on an experiment in which a coke previously drenched with iron chloride solution gave a combustibility of 50.9 per cent as compared with 21.9 per cent for the untreated coke.

Walker, Lewis, and McAdams<sup>59</sup> point out the important influence on combustibility of the thickness of the adhering gas films on the surface of the coke, and the rates of diffusion of the reacting gases and products of combustion through these films. The thickness of this film decreases as the rate of gas flow over the coke increases.

Perrott and Kinney<sup>60</sup> define combustibility of coke in terms of blast-furnace operation as follows: "The combustibility of fuel burned at the tuyeres is inversely proportional to the distance from the tuyeres at which oxygen and carbon dioxide have disappeared or, in other words, directly proportional to the space rate of disappearance of oxygen and carbon dioxide." They analyzed a large number of samples of gas obtained through water-cooled sampling tubes driven into the hearth through the tuyeres of 11 blast furnaces operating on cokes varying widely in physical characteristics. The results showed that combustion is complete at 32 to 40 in. in from the tuyeres and that these relatively small differences cannot be correlated with the differences in physical properties of the coke. Evidently the large differences observed in blast-furnace operation with different cokes are caused by other factors than the relative combustibility of cokes in the tuyere zone.

<sup>55</sup> *Brennstoff-Chem.*, **4** (1923), 273.

<sup>56</sup> *Ibid.*, **4** (1923), 312.

<sup>57</sup> *Trans. Am. Electrochem. Soc.*, **36** (1919), 91.

<sup>58</sup> *Brennstoff-Chem.*, **4** (1923), 312.

<sup>59</sup> "Principles of Chemical Engineering," McGraw-Hill Book Co., 1923.

<sup>60</sup> *Trans. Am. Inst. Mining Met. Eng.*, **69** (1923), 543.

## SULFUR IN COAL AND ITS CONVERSION IN CARBONIZATION

Powell<sup>61</sup> traces experimentally the reactions which the various forms of sulfur undergo during carbonization of coal. Between one-fourth and one-third of the original sulfur is driven off in the gas, principally as hydrogen sulfide, and to a small degree as carbon disulfide, thiophene, mercaptans, etc. The remainder is retained in the coke as ferrous sulfide and in other forms not combined with bases, usually termed *organic sulfur*. One-half of the pyritic sulfur remains in the coke as ferrous sulfide, and the other half passes off in the gas as hydrogen sulfide.

Important secondary reactions are the formation of carbon disulfide by the action of hydrogen sulfide on the red-hot coke, and the formation of hydrogen sulfide by the action of hydrogen on sulfur and ferrous sulfide of the hot coke. Wibaut<sup>62</sup> has pointed out that the "organic" sulfur in coke frequently occurs in quantities greater than the organic sulfur in the coal from which the coke is made, and concludes from experiments in which he carbonizes sugar to which some sulfur is added that the sulfur is chemically combined with the carbon in a compound which he calls *carbon sulfides*. Wibaut's data, however, show no stoichiometrical relationship between the carbon and the sulfur, and, as pointed out by Powell,<sup>63</sup> it might equally well apply if the sulfur were present as adsorbed sulfur, either free or in combined form, or as a solid solution of either free or combined sulfur.

From the standpoint of the phase rule, Powell made an extensive experimental study of the system carbon-sulfur, using sugar charcoal and pure sulfur for the components in some of the experiments, and coke from coal in other experiments. From these experiments he concludes that "the 'organic' sulfur occurs in two forms, (a) adsorbed free sulfur, and (b) sulfur in solid solution in the carbon or held on the surface of the carbon in such a manner that it is impossible by any known means to differentiate it from a solid solution." The adsorbed free sulfur slowly passes into solid solution when the coke is maintained at high temperatures.

<sup>61</sup> *J. Ind. Eng. Chem.*, **12** (1920), 1069.

<sup>62</sup> *Brennstoff-Chem.*, **3** (1922), 273.

<sup>63</sup> *J. Am. Chem. Soc.*, **45** (1923), 1.

Analyses<sup>64</sup> of five samples of various kinds of metallurgical and gas coke showed that from one-half to one-third of the sulfur of coke is in solid solution; from one-sixth to one-fifth is adsorbed as free sulfur; and the remainder is present as ferrous sulfide. Sulfate sulfur is usually absent, or present only in very small quantities.

The solid-solution sulfur probably remains in the coke during its descent in the blast furnace to the tuyere zone, where it is finally absorbed by the slag when the coke is burned;<sup>65</sup> but the sulfur present in coke as ferrous sulfide, together with the adsorbed free sulfur and sulfates, which are reduced to sulfides in the blast furnace, are in suitable form to be absorbed by the spongy iron.

**The Desulfurization of Coke.**—The great economic importance of discovering new methods of sulfur reduction in making available the higher sulfur coals for coke manufacture has led to trial of chemical methods of gas treatment during and subsequent to the coking process as well as the more common methods of water washing, air treatment, oil flotation, etc., as applied to the raw coal. An excellent historical review of these methods is given by Powell and Thompson,<sup>66</sup> who have made an extended experimental study of the desulfurization of coke by steam.

A number of investigators have succeeded in removing from 10 to 50 per cent of the total sulfur in coke by hydrogen or steam treatment of pulverized coke in small-scale laboratory tests. These workers, however, did not appreciate the importance of the different forms of sulfur in their studies. Powell and Thompson attacked the problem with a knowledge of the forms in which sulfur existed in coke and the reactions of these forms during gas treatment, and also the probable effect of the various forms remaining in the treated coke, on the iron in the blast furnace and the foundry cupola. They found that steaming was more beneficial than the reduction of total sulfur indicated, since the sulfur removed consisted almost entirely of sulfide sulfur and surface-adsorbed sulfur on the lumps of coke. These are the forms of sulfur, and not the "solid solution" form, which are easily absorbed by the iron. From 15 to 25 per cent of the total

<sup>64</sup> POWELL: *Ind. Eng. Chem.*, **15** (1923), 951.

<sup>65</sup> POWELL: *Trans. Am. Inst. Mining Met. Eng.*, **69** (1923), 587.

<sup>66</sup> Carnegie Institute Tech., *Bull.* **7** (1923), 3.

sulfur content of lump coke was removed by steaming from 2 to 4 hours at 750°C.

### COAL TAR

**Sources and General Characteristics.**—When coal is heated, without access of air, to a temperature of about 300°C., certain constituents of the coal begin to decompose, yielding gases and volatilized liquid products. At first relatively small quantities of gases and large quantities of liquid products are evolved; but as the temperature rises, the quantity of gases increases and that of liquid products decreases. The primary decomposition is completed between 500 and 550°. If the process is carried on at a temperature not to exceed 650°, it is termed "low-temperature carbonization," and when carried out above that temperature, it is called "high-temperature coking." The viscous, dark-colored liquid products constitute the crude tar of commerce, most of which comes from coke-oven plants, and coal and water gas works.

The composition of tar varies with the rank of the coal from which it is made and with the temperature to which it has been subjected during the distillation process. Thus, the higher the oxygen content of the coal, the higher the tar yield,<sup>67</sup> and the richer the tar in oxygenated compounds, such as phenols and cresols.<sup>68</sup> A higher yield of tar is obtained by carbonizing at low temperatures (400 to 650°). Low-temperature tar is characterized by a high tar acid content, absence of naphthalene and anthracene, and a small pitch residue.<sup>69</sup> It also contains naphthenes, and a larger amount of paraffins than high-temperature tar from coke ovens or gas works carbonizing at 950 to 1,100°. The differences between coke-oven and gas-works tar are small and not clearly defined, because both types of tar vary with the different carbonizing and condensing apparatus in use. Spilker<sup>70</sup>

<sup>67</sup> SPILKER, DITTMER and WEISTGERBER: "Kokerei und Teerprodukte der Steinkohle," 3d ed., Wilhelm Knapp, Halle, 1920.

<sup>68</sup> LEWES: "The Carbonization of Coal," John Allan & Co., London, 1912.

<sup>69</sup> GLUUD: "Die Tieftemperaturverkokung der Steinkohle," Wilhelm Knapp, Halle, 1921.

<sup>70</sup> *Lib. cit.*



gives the specific gravity of coke oven tar at 1.12 to 1.18 as compared with 1.18 to 1.25 for gas-works tar. The benzol content of coke-oven tar is usually low (under 0.5 per cent), whereas that from the gas works may contain as much as 1.2 per cent. Tar distillation yields, given as applying to both types of tar, are as follows:

Oily distillate:	PER CENT
Oil.....	35
Solid hydrocarbons.....	6
Pitch.....	55
Water and loss.....	4

Spilker names 100 compounds known to be present in coal tar, most of which belong to the following classes: phenols, nitrogen bases, aromatic hydrocarbons, unsaturated hydrocarbons, and cyclic non-benzenoid hydrocarbons. All of the compounds in tar have not been isolated, in particular the neutral oils<sup>71</sup> "occurring in its distillation between the phenols and naphthalene on the one hand and anthracene oil on the other." Complete knowledge is lacking on the composition of the anthracene oils and little is known of the pitch compounds.

Weiss and Downs<sup>72</sup> analyzed a vacuum-distilled sample of mixed coke-oven tars and found its composition to be as follows:

	PER CENT BY WEIGHT OF DRY TAR
Light oil:	
Crude benzene and toluene.....	0.3
Coumarone, indene, etc.....	0.6
Xylenes, cumenes, and isomers.....	1.1
Middle and heavy oils:	
Naphthalene.....	10.9
Unidentified oils in range of naphthalene and methyl- naphthalenes.....	1.7
$\alpha$ -monomethylnaphthalene.....	1.0
$\beta$ -monomethylnaphthalene.....	1.5
Dimethylnaphthalenes.....	3.4
Acenaphthene.....	1.4
Unidentified oil in range of acenaphthene.....	1.0
Fluorene.....	1.6
Unidentified oil in range of fluorene.....	1.2

<sup>71</sup> LUNGE: "Coal Tar and Ammonia," Guerney & Jackson, London 1909

<sup>72</sup> *Ind. Eng. Chem.*, **15** (1923), 1022.

	PER CENT BY WEIGHT OF DRY TAR
Anthracene oil:	
Phenanthrene.....	4.0
Anthracene.....	1.1
Carbazol and kindred non-basic nitrogen-containing bodies.....	2.3
Unidentified oils, anthracene range.....	5.4
Phenols.....	0.7
Phenols homologs (largely cresols and xylenols).....	1.5
Tar bases (mostly pyridine, picolines, lutidines, quino- lines, and acridine).....	2.3
Yellow solids of pitch oils.....	0.6
Pitch greases.....	6.4
Resinous bodies.....	5.3
Pitch (460°F. melting point).....	44.7
Total.....	100.0

These authors conclude that there are comparatively few compounds existing in tar, in appreciable amount.

The water in tar is held as a more or less stable emulsion dispersed in fine droplets in the tar, the condition for stabilization being brought about by the presence of certain tar constituents which act as emulsifying agents. Free carbon, hydrocarbons of high molecular weight, and possibly other compounds are also dispersed in the tar. Posnjak<sup>73</sup> found that polymers of styrol ( $C_8H_8$ ) can be dispersed in the unpolymerized styrol itself.

An instructive series of researches on the amount and composition of primary tar obtainable from various kinds of coal has been carried out by Fischer and his associates<sup>74</sup> at the Kaiser-Wilhelm Institut für Kohlenforschung, Mülheim, Ruhr. According to Gluud, primary tar is a mixture of phenols and hydrocarbons, the hydrocarbons being chiefly paraffins, olefins and naphthenes. Benzene, naphthalene, and anthracene are absent.

The ordinary coke-oven and gas-works tar is simply overheated primary tar. The effect of high temperature is to decompose the paraffine first into olefins, which go to diolefins and finally to aro-

<sup>73</sup> Dissertation Leipzig, 1910.

<sup>74</sup> FISCHER and GLUUD: *Ges. Abhandl. Kenntnis Kohle*, **1** (1915-16), 114; **2** (1917), 215; GLUUD: "Die Tieftemperaturverkokung der Steinkohle," Wm. Knapp, Halle, 1921; *Ges. Abhandl. Kenntnis Kohle*, **3** (1918), 14.

matic hydrocarbons; light paraffins, which are gaseous (principally methane), are likewise decomposition products of the primary paraffins. Naphthenes split off hydrogen and form aromatic hydrocarbons. Naphthalene and anthracene are also formed, probably by the condensation of simpler aromatic compounds and olefins. A physical indication of the change brought about in tar by heat is the progressive increase in specific gravity from about 1.0 to 1.20. Fischer<sup>75</sup> considers that the chief sources of benzene and its homologues in ordinary tar are the phenols of the primary tar. He finds, that, besides the reduction of the hydroxyl groups, there is a tendency toward splitting off of the methyl groups, from the cresols, for example, with the formation of benzene.

**Cumarone Resins.**—The cumarone resins, which consist largely

of cumarone  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CH} \\ \diagdown \text{O} \end{array} \text{CH}$ , indene  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CH} \\ \diagdown \text{CH}_2 \end{array} \text{CH}$ , and

their homologues are of special interest to the colloid chemist because of their industrial application in lac and varnish, impregnating, and print-color industries. They are recovered<sup>76</sup> in the distillation residues of light oil after it has been freed from acids and bases and washed with from 4 to 10 per cent concentrated sulfuric acid. Characteristic yields are 2.64 per cent of the light oil or 0.2 per cent of the crude tar. The total amount of these resins, all grades included, produced in Germany was 6,000 tons in 1914, and 11,000 tons in 1917. Quality of cumarone resins is determined largely by their color, which in the best grades is *water white*, and by their consistency, which must conform to the use for which the grade is intended. Good color is obtained by exercise of care in washing with sulfuric acid, and consistency is controlled largely by the heat treatment of the resin-containing residues. The higher the temperature, the harder the resin obtained.

Glud and Breur<sup>77</sup> obtained cumarone resin from the tar acids

<sup>75</sup> Brennstoff-Chem., **1** (1920), 22; Ges. Abhandl. Kenntnis Kohle, **4** (1919), 373.

<sup>76</sup> GLASER: Brennstoff-Chem., **2** (1921), 99.

<sup>77</sup> Ges. Abhandl. Kenntnis Kohle, **3** (1918), 238.

of low-temperature tar by subjecting them to a cracking process. The yield was 0.1 per cent of the crude tar.

**Tar Mists.**—Tar mists are formed in carbonizing coal very soon after the tar is generated.<sup>78</sup> There probably is no true vaporization of the tar. Rapid evolution of gases coincident with the formation of liquid tar ejects small bubbles of the latter before vaporization takes place. These mists have been removed with Cottrell precipitators, in the Bureau of Mines Laboratory, at temperatures (600°C.) above those required for carbonization. The composition of the tar mist is practically the same at all points in the condensing system. Fractional condensation obviously cannot be applied to mists.

**Handling of Mists in Coke-oven and Gas-works Practice.**—In practice, tar is almost universally removed from the gas by progressive cooling and scrubbing, combined with the use of some form of mechanical extractor, such as the Otto-Hilgenstock or Pelouze-Aoudin. In the latter device the gas is passed at high velocity through a series of perforated bells impinging the tar droplets on flat metallic plates, where they are coalesced. The slots or holes in the bells are staggered so that the direction of the gas flow is changed suddenly and the high inertia of the drops as compared with that of the gas causes the drops to be deflected against flat surfaces of succeeding bells. A number of devices based on the centrifugal principle have also been proposed from time to time.

Gas-works operators favor slow cooling of the gas and separation of the tar in progressive stages, because if the tar is removed too quickly it will carry with it more of the light oil vapors, which is not desired when the gas is sold under a high B.T.U. specification. Any tar mist that passes the condensing and scrubbing system clogs the oxide purifiers, thereby lowering their efficiency, and, in coke-oven plants, contaminates the ammonium sulfate.

Cottrell precipitators will remove tar mist from gases. This method<sup>79</sup> consists in passing a high-tension, direct electric current through a stream of tar-laden gas carried in a suitable conduit, which may be a cylindrical iron pipe. In the center of the pipe

<sup>78</sup> BANCROFT: "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921.

<sup>79</sup> COTTRELL: *J. Ind. Eng. Chem.*, **3** (1911), 542.



an insulated cathode, which usually consists of a squirrel cage of fine wires or sometimes a single fine wire, serves to conduct the silent discharge to the suspended particles. These particles carry the charge to the walls of the tube, which serve as the anode, where they are relieved of their charge and are themselves deposited. White, Rowley, and Wirth<sup>80</sup> experimented with an 8-in. U-pipe precipitator containing a "squirrel-cage" cathode. They passed raw coal gas, at 75 to 150°F., through the apparatus at the rate of 24,000 cu. ft. per hour. The voltage was 20,000 and the energy supply about 0.2 kw., which completely precipitated the tar mist. The estimated installation cost for apparatus of this capacity was \$300. White claims the following advantages for the method:

1. Gas freed from tar at any desired temperature.
2. A high heating value maintained for the gas (by working at high temperatures the light oil vapors could be prevented from condensing).
3. Oil washers for naphthalene can precede the precipitator.
4. Clean ammonia; easy application of the direct recovery process.
5. Easy purification.

The electrical precipitation method has not yet come into commercial use. It may be used to advantage for complete removal of tar mists in the laboratory carbonization of coal.

**Tar Emulsions.**—Emulsions are formed during the condensation of tar and water in the destructive distillation of coal. Emulsions of tar in water, containing a high percentage of water, are unstable and the water is separated in practice by simply allowing the tar to settle out by gravity in tar wells. The residual water amounts to only a few per cent and this is removed by gradually heating the tar; the water distills with the light oils and is easily separated by gravity. Stable emulsions of water in tar are often formed in the manufacture of water-gas and in low-temperature carbonization. Water-gas tar emulsions consist of very small droplets of water dispersed in tar.

Odell<sup>81</sup> considers finely divided carbon the emulsifying agent in these emulsions. He found that there was an optimum amount

<sup>80</sup> *J. Gas Lighting*, **127** (1914), 719.

<sup>81</sup> *Am. Gas Assoc. Monthly*, **3** (1921), 305; **4** (1922), 136.

of carbon required for each particular tar to produce an emulsion of maximum stability. Increasing the amount of carbon above the optimum tended to break the emulsion, and adding a large amount of carbon produced fairly complete separation. Evidently, the carbon is adsorbed in the interface, lowering the surface tension on the tar side. Similar emulsions have been made of water in kerosene, by Moore<sup>82</sup> and by Schlaepfer.<sup>83</sup> An obvious remedy in preventing water-gas tar emulsions is to avoid the production of finely divided carbon in the gas by a suitable adjustment of operating conditions.

**Removal of Light-oil Vapors from Coal Gas.**—Light-oil vapors are absorbed from gas by spraying the gas in tall towers with petroleum oil (straw oil) or cresol. The light oil is recovered from the oil solution by steam distillation and condensation. Englehardt<sup>84</sup> describes the recovery of light oils in certain German gas works by adsorption in wood charcoal; 1 kg. of charcoal absorbs 400 g. of light oil. The yields are said to be 10 to 20 per cent larger than those obtained by the usual wash-oil methods, and it is further claimed that fractional separation of the light oils is obtained by using a series of charcoal adsorbers.

Activated charcoal has been applied to the determination of gasoline in natural gas,<sup>85</sup> and a commercial process of high efficiency for recovering casinghead gasoline has been developed<sup>86</sup> and put into industrial use. Activated charcoal has been used satisfactorily in the Bureau of Mines Laboratory for several years for determining the light-oil content of coal. Berl and Andress<sup>87</sup> also claim that the charcoal adsorption method is the simplest and most accurate method known for the determination of light oils in illuminating and coke-oven gas.

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<sup>82</sup> *J. Am. Chem. Soc.*, **41** (1919), 940.

<sup>83</sup> *J. Chem. Soc.*, **113** (1918), 522.

<sup>84</sup> *Gas u. Wasserfach*, **64** (1921), 205.

<sup>85</sup> BANCROFT: "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921; OBERFELL, SHINKLE and MESERVE: *J. Ind. Eng. Chem.*, **11** (1919), 197.

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## CHAPTER XXII

### COLLOIDS AND FUEL

By

S. EDWARD SHEPPARD

In 1917 in a preliminary report on the problem of colloidal fuels,<sup>1</sup> the writer wrote as follows:

**1. General Problem.**—Quite apart from many specific phases of the obtaining and refining of raw materials, the fuel problem has a general colloidal side, at least in respect of the part played by subdivision of material.

It is worth noting at this point that much of the advance in inner ballistics, in the application of explosives, has depended upon the adjustment of the grain size of the material, in conjunction with proper homogenization.

In the case of *gaseous* fuels, whether used for internal combustion (explosion) motors, or for external combustion (steam raising), there are not any direct aspects of the problem obviously contingent to the study of colloids. A gas has in the nature of things an enormous inner homogeneous subdivision, a molecular dispersity.

For *liquid* and *solid* fuels, however, the colloid aspect is immediate. For internal combustion engines the combustible liquid is "atomized" mechanically, the fine subdivision being necessary for rapid formation of an explosive mixture with air. Similarly, atomization is resorted to in the case of fuel oils in steam raising, etc. The initial reaction system here is:

Inner (disperse) phase	Outer (dispersing) phase
Oil	(Vapor) Air

or, in more familiar terms, we have an *oil-mist*, a suspension of oil droplets in air.

From the colloid standpoint the only radical question which suggests itself here is whether it would be advantageous to reverse the conditions of dispersion, that is, to produce as the initial reaction system an *oil-froth* or *foam*, a cellular structure with oil walls and air-oil vapor contents:

<sup>1</sup> Report to the Submarine Defense Association.



Inner (disperse) phase	Outer (dispersing) phase
Air	(Vapor) Oil

Leaving the question of internal combustion for that of fuel proper, we have to note that the advantage of liquid fuel depends largely, though not necessarily entirely, upon its ready subdivisibility, readily allowing a very complete admixture with air.

Approach to this from the side of solids, especially coal, has been made in the increasing use of powdered coal. The coal is reduced in these processes to a powder passing 200 to 260 mesh. What this means is that a 1-in. cube, pulverized so that 85 per cent passes a 200-mesh screen, will produce 35,500,000 particles. Such a 1-in. cube exposes a surface of 6 sq. in., but when thus pulverized there will be exposed more than 1,872 sq. in., so that the *dispersity*, or ratio of surface to volume, has been increased over 300 times.

While greatly increased combustion efficiency is obtained in this way, there is still certain progress possible. The highest efficiency would be reached by subdivision of the coal to ultramicroscopic or colloidal dimensions, in the narrow sense. That would mean subdivision such that the diameters of the particles were less than  $1\mu$ , or 0.001 mm., or 0.0004 in., and an increase in the dispersity from the 1-in. cube size of more than 10,000.

It has been shown in a multitude of cases that the reactivity and catalytic effect of a subdivided solid attains its maximum for the

colloidal dimensions, between  $0.1\mu = \frac{1}{10,000}$  mm. and  $1\mu\mu = \frac{1}{1,000,000}$

mm. (cf. Wo. OSTWALD, "Die Welt der Vernachlässigten Dimensionen," p. 48). But, while increased efficiency seems probable, could this subdivision be attained, this would seem at first sight only to increase a disadvantage already inherent with powdered coal. This is the fact that the tendency to aerial oxidation, to loss of fuel value on keeping, and danger of spontaneous combustion is greatly increased by such fine subdivision. With this also increases the danger of explosion of air-coal-dust mixtures.

These disadvantages could be eliminated if the subdivided coal were suspended in an indifferent but combustible liquid, and the composite system used as a *liquid fuel*.

At present it is doubtful if the reduction of coal mechanically to colloidal dimensions is practicable, although a considerable step in advance of present dimensions would no doubt be possible if any advantage could be shown. This advantage exists when suspension in mineral oils enters into the question. This advance to the colloid

subdivision is desirable, for reasons which will shortly appear, over and above those given.

If not obtainable mechanically, could this be completed by other means? It appears possible that a chemical disintegration method, analogous to Kuzel's method for producing colloidal tungsten, might be effective. Taking advantage of the straticchemical character of coal, considered as a combination of condensed lignocelluloses with resinified hydrocarbons, or as a solid solution of the following components:

Carbohydrates, condensed

Hydrocarbons, mostly saturated, but some unsaturated

Inorganic oxides

Sulfur- and nitrogen-containing bodies

it appears feasible that, under alternating attack of chlorine upon coal powder suspended in concentrated hydrochloric acid, and of an alkaline solution, disintegration of the coal to a colloidal slime might be attained. The slime or aqua-dag so obtained could then be converted into oil-dag by pugging with mineral oils, as in Atcheson graphite.

Leaving this speculative field, however, there exists the more immediate possibility of combining mechanically powdered coal with mineral oil to form a composite fuel, which, in view of the conditions essential to production and stability, may be properly termed a colloidal fuel.

**2. Special Case.**—The special case we have to consider, then, is the combination of finely powdered coal with mineral oil to form a liquid fuel, in which a large proportion of oil is replaced by coal.

The writer has reproduced this verbatim because, except on certain details, it still presents both the general and special problem under discussion. The fact that such raw materials for fuel as coal, oil, and shales are colloidal in character is more or less generally realized. The further fact that the refining of these to specific fractional products involves a multitude of colloid chemical problems is only gradually coming to be recognized.<sup>2</sup> Still nearer to and below the threshold of general engineering consciousness is realization of the importance of colloid chemical factors in the utilization and economizing of fuel products in their final service. It is solely with certain phases of this last aspect that this article deals. They bear on the special problem referred to in the quotation. But it seems desirable to state that, in the vast and complicated problem of fuel con-

<sup>2</sup> Recognition of colloid problems in refining crude oil, in flotation processes for de-ashing coal, etc.

servation, any contribution such as that briefly reviewed here should be properly considered in relation to others and to the general nexus.

The following outline indicates some, though not all, of the specific possibilities in colloidizing the fuel problem:

1. Production of stable suspensions of coal powders in fuel oils of medium viscosity (150 to 200 Engler), stabilized by protective colloids.

2. Production of coal and carbon dispersions of colloid dimensions in oils of lower viscosity (100 Engler), stabilization assisted by protective colloids.

3. Semi-colloid dispersions of coal by solvent peptization by tars and tar distillates in oils and mixtures of oils and tars.

4. Chemical peptization of powdered coals by hydrous or anhydrous oxidizing agents, followed by amalgamation to plastic fuels or stabilization to colloidal fuels.

5. Hydrogenation of coal, of mechanical mixtures of coal and oil, of colloid composites of coal and oil, or of coal, tars, and oils—including pitches and cognate materials.

Of these, the first two overlap, but distinction is advisable, on account of the practical difficulties in colloid milling. Although the advent of the Plauson colloid mill (*q.v.*) has brought this perceptibly nearer to industrial significance, much remains in the matter of economical operation.<sup>3</sup> But it may be noted here that, in order that the *fluidity*, or, more correctly, the *mobility*, in Bingham's sense,<sup>4</sup> of such composite fuels may not become too low, the dispersity of the solid phase must be correlated to the viscosity of the liquid phase. To secure economically significant results, the percentage of dispersed solid phase, *e.g.*, coal or carbon, must be of the order of 30 per cent by weight and upwards. With oils of high viscosity (200° Engler), increasing dispersity of the whole of the solid phase to colloid dimensions brings the mobility down too low for many purposes. This is illustrated in Fig. 1.

The possibilities noted under (1), (2), and (3) were considered and developed rather fully during and following the year 1917,

<sup>3</sup> BLACK, B.: *Z. angew. Chem.*, (1921), 25.

<sup>4</sup> Cf. BINGHAM, E. C.; "Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922.

at first by the Submarine Defense Association of New York City, in cooperation with the Research Laboratory of the Eastman Kodak Company, later by Lindon W. Bates,<sup>5</sup> Chairman of the Engineering Division of the Association. The possibilities indicated under (4) have been exploited, in regard to the amalga-

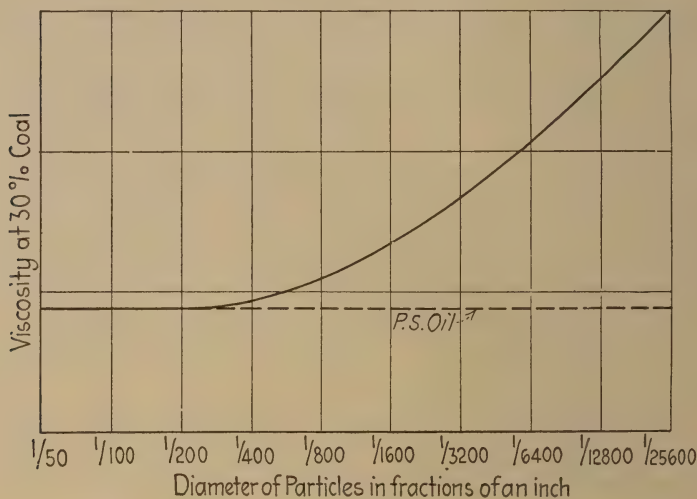


FIG. 1.—Effect of subdivision of coal on viscosity of fuel.

mation of coal powders with oil from hydrous pastes, by the Trent Plastic Fuels developments.<sup>6</sup> Also, considerable independent progress has been made in regard to the chemical disintegration of coal by sulfur dioxide, chlorine, etc. Finally, a beginning in regard to the possibilities noted under (5) has been made by Bergius—in Germany.

#### STABILIZING COAL SUSPENSIONS IN OIL

Early experiments in 1917 with suspensions of both anthracite and bituminous coals in fuel oils of viscosity varying from 20 to 200° Engler at 20°C. showed that coal pulverized to pass 200

<sup>5</sup> See bibliographic references at end of chapter.

<sup>6</sup> Cf. bibliography at end of chapter.



mesh settled out very much less rapidly than indicated by Stokes' law. The deviations were assigned to:

1. Non-spherical form of the particles.
2. Increased inner friction and "plasticity" of the composites.
3. Adsorption of oil or oil components to coal.

Although this deviation in the direction of increased stability exists it is not sufficient for practical purposes, where the life of the suspension must be from months to years, according to requirements. Oils have been graded in the past chiefly by specific gravity, generally expressed in degrees Baumé, but this gives no clue to the great variations of viscosity which exist, and which cover a range of 1 to 30,000 or even more.

It is generally considered<sup>7</sup> that, for effective atomization by mechanical burners, the viscosity must not be higher than about 8° Engler. This is achieved for the more viscous oils by preheating to this point, beyond which no marked advantage is secured. This reduction of viscosity by preheating must not involve a temperature higher than the flash point of the oil. Because of the high value of the volatile portions of crude oils for internal combustion engines, the residuals available for fuel oil have generally quite high flash points. In fact, due to the tendency to put as much of the heavier fractions through "cracking" processes as possible, the residuals available for straight fuel oil are always tending to be diminished; some of the residuals from this process, containing "free carbon" and rated as tars, are quite suitable for colloidal fuel production, since the carbon and pitch can be stabilized in the same way as suspended coal particles. British naval specifications for the flash point were: not lower than 175°F. closed cup or 200°F. open cup, and the U. S. A. naval specifications are now practically the same. Hence, a composite fuel would have to have a viscosity of 8° Engler at a temperature lower than a flash point of 175°F. closed cup.

Keeping to this, the generally dominant factors in making such colloidal fuels as noted under (1) and (2) are:

1. To secure a temperature coefficient of viscosity permitting this minimum at practicable preheat temperatures.

<sup>7</sup> Cf. PEABODY, F. A.: "Oil Fuel," Trans. Internat. Eng. Congress, 1915.

2. To secure a maximum viscosity within limits of pumpability, allowing some degree of preheating in this.

3. To find protective colloids adequately stabilizing the coal or carbon suspensions within permissible viscosity limits.

In regard to securing oil base of the requisite viscosity, much greater latitude is possible for blending and "cutting back" than is possible with fuel oils alone. This is because the stratifications and separations which complicate the problem of straight oil blending are greatly reduced and almost automatically overcome by the process of colloidizing. It will be remembered that Pickering has shown the stabilizing effect of finely divided particles upon emulsions of oils with water. As between stratifying mineral oil fractions, the interfacial tensions to be overcome are much less, and the presence of 30 per cent or more of finely divided coal or carbon readily effects this. In fact, this action was found later to secure a considerable degree of emulsion stability for mixtures of mineral oil with coal tars and gas tars, although here the question becomes complicated by the incidence of peptization of coal by coal tars noted later.

True stabilization of these composites, types (1) and (2), can be brought about by the use of protective colloids; the most suitable for this purpose were found to be soaps, and particularly the calcium soaps. In most of the earlier colloidal fuels, calcium soaps derived from rosin were used. By proper choice of ingredients and processing, a protective colloid, termed the "fixateur," was prepared,<sup>8</sup> by which upwards of 30 per cent of coal pulverized to 200 mesh could be stably suspended for periods extending to 18 months and more, with only 1 per cent of soap.

The colloid chemistry of soap-thickened oils has been frequently discussed, but the technology of their production still retains many unexplained details. The author has pointed out certain possible explanations of their nature as essentially plastic systems.<sup>9</sup> In view of the work of McBain and his collaborators, on soaps, some of these lacunae may now be susceptible of explanation. Undoubtedly, the sols and gels of these soaps contain

<sup>8</sup> See bibliography at end of chapter.

<sup>9</sup> *J. Ind. Eng. Chem.*, **13** (1921), 37.

fibrils formed by the association of soap molecules.<sup>10</sup> This association, and the adsorption of the dispersing medium, are very possibly dominated by the conditions of molecular orientation discovered by Hardy, Harkins, and Langmuir, but, in any case, systems are formed of relatively high mobility, but with appreciably high "yield points."

While soaps derived from rosin have been largely used, others are available, including those derived from naphthenic acids, and acids of high molecular weight produced by processes of refining and oxidizing mineral oils themselves.

### PEPTIZATION OF COALS AND PITCHES

In the course of the work on the development of colloidal fuels it was found<sup>11</sup> that the free carbon and pitch in residual oils, such as pressure still tars and Mexican oils, could be peptized by the addition of certain coal tar distillates rich in these. This treatment greatly reduced the viscosity, in addition to stabilizing the product. It was found that, under the action of heat, suspensions of coal, pulverized to 200 mesh, in coal tars, in creosote oils, or mixtures of these with oil, became peptized. In the case of suspensions of 30 per cent or more, this led to great increase of viscosity, and it was evident that the peptization of coal here was related to the known process of solvent disintegration of coals.<sup>12</sup> This process alone permits composites of mineral oil, tar, and coal to be formed, containing upwards of 30 per cent coal, of 200 mesh, and tar to the extent of 20 per cent, stable for periods of weeks and months. Greater stability, *i.e.*, longer life, may be secured by a combination with the process which utilizes mechanical milling and protective colloids, to which the foregoing affords an effective complement, increasing the flexibility and the economy which is possible.

It may be said here that there is a wide field for colloid chemical research, both analytical and synthetic, open in the study of these peptization reactions. Ultramicroscopic observations have

<sup>10</sup> McBAIN, J. W.: The Study of Soap Solutions. *Chemistry and Industry*, (1923), 615.

<sup>11</sup> Cf. SHEPPARD, S. E.: *J. Ind. Eng. Chem.*, **13** (1921), 37.

<sup>12</sup> Cf. STOKES, M. E. and WHEELER, R. V.: Constitution of coal, *Dept. Sci. Ind. Res. Gt. Britain*.

shown that increase of dispersity is produced, but little is known of the chemical and physical relations involved. Further, a study of the plastic and viscous properties on the lines developed by E. C. Bingham would undoubtedly yield results of great interest and value.

The three stages of attack:

Mechanical Comminution  $\rightarrow$  Solvent Peptization  $\rightarrow$  Chemical Peptization

result in progressively more profound disintegration, but they can be used to support and relay each other effectively.

### PROCESSING COLLOIDAL FUELS

The machinery for compounding these fuels is of a relatively simple character. It consists of mills for pulverizing coal, coke, etc.; mills for wet grinding; mixing kettles and autoclaves for preparing fixateurs; peptizing and hydrogenating, storage, and

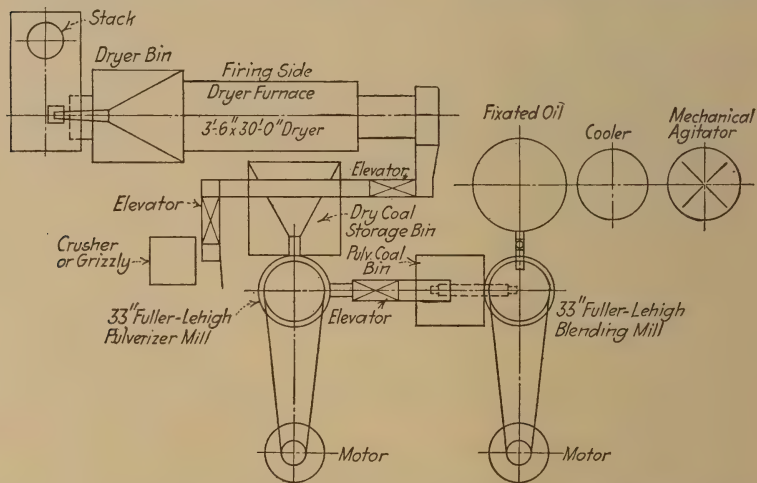


FIG. 2.—Proposed arrangement of the colloid fuel plant. (*Submarine Defense Association*).

blending tanks; heavy-duty pumps. Plants operating on the production of "synthetic heavy fuels" will, no doubt, be associated with distillation and refining plants, so that "synthetic light fuels" production can be economically combined therewith.



A diagrammatic layout for a simple colloidal fuel plant is shown in Fig. 2. De-ashing processes are readily combined with the colloidizing processes, and are an important adjunct where coals of high ash content only are available, or where it is essential to secure a minimum mineral matter.

### GENERAL PROPERTIES

In conclusion, the properties of such colloidal fuels as have been made and tested may be briefly recorded:

1. Liquid or semi-liquid, can be atomized for combustion, like fuel oil.

2. Specific gravity generally higher than water. Specific gravity given by law of mixtures, *e.g.*, of mixture of coal and oil

$$\text{Sp. gr.} = \frac{100 \times \text{sp. gr. coal} \times \text{sp. gr. oil}}{\% \text{ oil} \times \text{sp. gr. coal} + \% \text{ coal} \times \text{sp. gr. oil}}$$

With more complex systems, with advanced peptization or chemical attack, deviations will occur. The increased specific gravity over water permits such composites to be stored under water seal, and increases protection from fire hazard.

3. Calorific value per unit weight lower than straight fuel oils, generally also given by law of mixtures.

4. Calorific value per unit volume generally equal to, or higher than, that of straight fuel oils, possible by use of coals of high carbon content and high density.

5. Combustion efficiency found by service trials, both on sea and land, to be equal to that of straight fuel oil. Can be used with mechanical compressed air or steam atomizers. High-grade colloidal fuels with negligible ash content are practicable for Diesel and semi-Diesel types of internal combustion engines.

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## CHAPTER XXIII

### THE PRECIPITATION OF SMOKE AND OTHER SUSPENSIDS IN GASES

By

WILLIAM W. STRONG

"Gases" consist of molecules, atoms, electrons, or combinations of these in characteristic free gaseous motion. Suspensoids in gases consist of "particles" suspended and constitute the smokes, mists, fumes fogs, clouds, hazes, and dusts. Suspensoids are almost invariably opaque or translucent to light and this quality is due to the solid or liquid character of the suspensoid "particles." If the "particles" are sufficiently small, they exhibit the Brownian motion. Electrically charged "particles" are called "ions" and can be removed from a gas by the action of an electric field. Magnetic "particles" can be removed from a gas by the action of a magnetic field. Sufficiently large "particles" can always be removed from a gas by mechanical means, such as screening, filtering, centrifuging or settling.

In precipitating suspensoids, the term "fluid" may be used to include gases and liquids. The cleaning of a fluid is effected by the action of precipitating ( $P$ ) forces, such as the mechanical forces  $F$ , the magnetic forces  $H$ , the force of gravity  $G$ , the electrical forces  $E$ , the centrifugal forces  $F_c$ . In all processes of separation of "particles" from fluids, the separating force quickly gives the "particle" a velocity  $v$  such that the frictional ( $F_f$ ) forces generated by the motion of the particle through the fluid balance the external force. This condition is described by the law of Stokes. If  $\pi = 3.1416$ ,  $\mu$  the coefficient of viscosity of the gas,  $a$  the radius of the particle, and  $d$  the density of the "particle," then the velocity  $V$  of precipitation is given as follows:

$$\Sigma P = F_f = 6\pi\mu avd = \Sigma F + \Sigma H + \Sigma G + \Sigma E + \Sigma F_c. \quad (1)$$



In the oil-drop method of determining the charge of the electron, Millikan has shown that the law of Stokes is expressed more accurately, for gases, in the form

$$F_f \left( 1 + A \frac{\lambda}{a} \right) = F_f \left( 1 + \frac{b}{pa} \right) = b\pi\mu avd$$

where  $A$  and  $b$  are constants,  $p$  the pressure of the gas,  $\lambda$  the mean free path of the gas.  $A$  varies for different gases.<sup>1</sup>

The description and the measurement of the "amount" of suspensoid in a gas have not yet been standardized in engineering practice, for the reason that the opaqueness and the weight of the suspensoid "particles" depend upon the kind of matter in the "particles," their number, physical condition, and size. The size of the suspensoid "particles" is seldom if ever uniform. The nature of the electrical double layer about the "particle" is also very variable. Giving the number of "particles" per unit volume of the gas does not, therefore, uniquely describe a suspensoid unless it is uniform in structure. In the case of fumes containing valuable compounds it is common to describe the suspensoid as containing so many grains or grams weight of matter per unit volume of the gas. As the electrical precipitation of fumes takes place at comparatively high temperatures, it is customary to give the temperature of the gas and then to state the weight of suspensoid per unit volume of the gas at the standard temperature of the gas, say 0°C. If the suspensoid is black, as is soft coal smoke, its density is roughly its blackness; usually no mention is made of the thickness of the smoke or the light conditions involved. On the Ringelmann scale very dense black smoke is No. 6, and this grades gradually into No. 1, which is a very light smoke. Perhaps eventually the opacity of the suspensoid can be quickly determined optically, while a sample that has been passed through a gas meter and an electrical precipitator may have its weight per unit volume of gas determined.

<sup>1</sup> See *Phys. Rev.* (May, 1923), 550, 564.

THE LIFE HISTORY OF THE SUSPENSOID "PARTICLES"<sup>2</sup>

Perhaps the secret of colloidal chemistry will be discovered, as isotopes and charged droplets are now controlled, by the magnetic, electrical, and the mechanical forces. If we knew the life history of the birth and the growth of the smoke "particles" or a zinc oxide fume crystal, if we knew the atomic and the molecular forces that are effective at the surface of "particles," we would have made a tremendous advance in the region between atomic chemistry and microscopic mechanics. In the process of electrical precipitation one of the most important steps is that of the aggregation of the "particles" and the ions and, finally, the discharge of the "particles." At the same time various chemical reactions take place, such as the production of ozone, oxides of nitrogen, active chlorine, active nitrogen, the claimed production of gasoline from natural gas, etc. Many of these phenomena have little if any commercial value, but they will have great theoretical value.

## THE CLEANING OF GASES BY SCREENING AND FILTRATION

This process of removing suspensoids from gases is usually treated as mechanical. Recent investigations in the removal of zinc oxides in bag houses indicate that in certain cases the electrical forces play an important rôle. For certain fumes and dusts, extremely fine "particles" are removed in bag houses. Another example is that of air filters for cleaning air for turbo-generators (and similar machinery), which consist of metal cylinders covered with an oily liquid filling the filter cells.

## THE CLEANING OF GASES BY CENTRIFUGING

Centrifuging is well suited for removing relatively large suspensoid "particles," such as cinders, from gases. The "acting"

<sup>2</sup> The term "particle" is set in quotation marks to emphasize the indefiniteness of its properties. In a thunderstorm, or in a gas subject to the C. T. R. Wilson cloud expansion, a "particle" may grow from an infinitesimal ion or "nucleus" into a liquid drop in a short fraction of a second. In the cataclysm of the electrical precipitation process the "particle" is far more variable as regards shape, size, electrical charge, and the nature of its molecular surface layer.

force is called the "centrifugal" force  $C$ . The centrifugal process is also frequently used in flues where the direction of the smoke or fume flow is suddenly changed. On the other hand, the electrical precipitation processes are especially suited for the removal of very fine suspensoid "particles." In the near future it is quite likely that a combination of these two methods will be found to be very effective and will result in much more compact apparatus than is now used. The start along this line has been made by McGee and Nesbit.<sup>3</sup> A problem in connection with this apparatus is that of complete adjustment and control so as to obtain a maximum efficiency; the rotatory motion of the gas to be cleaned and the voltage of the electrical discharge have to be properly related. Here

$$P = C + F_e = F_f \quad (2)$$

#### THE CLEANING OF GASES BY SETTLING

The most stupendous precipitation of suspensoids from gases which we witness is that of the cleaning of the air by the settling of dust, fume, and smoke and by the fall of rain and snow. In the formation of rain, and especially during thunderstorms, we have phenomena involving electrical as well as gravity precipitation. Large settling chambers are used on a commercial scale for removing fumes, examples of which are the large settling chambers at Great Falls and Anaconda, Montana.

In the above method for cleaning gases, the ease of cleaning depends largely upon the size and the mass of the "particles." Very fine "particles" are removed very slowly from gases by the above methods. If the efficiency of cleaning is defined in terms of the energy required or work  $W$  done, then the slower the cleaning, the less the work required. If there are  $S$  suspensoid "particles" per unit volume, a volume  $V$  to be cleaned, and each suspensoid "particle" is moved a distance  $l$  so as to clean the gas, then from (1)

$$W = \Sigma V S F_f l = \Sigma V S l (b \pi \mu a v d) \quad (3)$$

The less the value of  $v$ , the less the work required. Processes such as centrifuging and electrical precipitation require much

<sup>3</sup> See U. S. patents 1372710; 1381719; 1371995; 1440886; 1440887; 1444845.

more energy than the settling processes. In practice, however, it is very important not to obstruct the draft in a flue or chimney, so that the matter of the efficiency of  $W$  seldom has any technical application. From the appearance of  $a$  in (2) it follows that it requires much less work to remove a given weight of suspenoid if it is in large "particles" than if it is in a very finely divided state. The filter and screen are efficient because  $l$  is made small.

In the process of electrical precipitation<sup>4</sup> fine suspenoid "particles" are removed from a gas about as effectively as the large "particles." For this reason, the electrical processes have long been suggested for the removal of fogs and mists in front of trains, boats, and even over large city areas. In other problems it has actually been found possible to aggregate small "particles" and then let the large "particles" fall from the gas. The problem of removing fogs and mists has not been solved because it is impracticable to place high voltage wires in front of trolley cars or boats or in streets. It is reported that Bancroft and Warren<sup>5</sup> have succeeded in precipitating rain by flying over the cloud in an aeroplane and distributing electrified sand upon the cloud from the aeroplane. The work was done on the McCook Aviation Field Dayton, Ohio, in the spring of 1923. The sand was charged electrically opposite to that of the natural charge of the rain drops and was of 150 mesh. An aeroplane carrying 80 lb. of sand was reported to clear large clouds in 10 minutes. It is quite likely that methods of this kind will find application when the clouds are fairly dense and partially electrified, though the popular view that electrical precipitation will become generally used to produce rain is doubtful.

#### THE CLEANING OF GASES BY IONIZATION AND THE ELECTRIC FIELD

In this method the gas, and subsequently the suspenoid "particles," are ionized or electrically charged and are then removed from the gas by the force of the electric field. This

<sup>4</sup> For a very general bibliography of smoke and smoke prevention see *Bull.* no. 2, Smoke investigation, Mellon Inst. Ind. Res., Univ. of Pittsburgh, 1913.

<sup>5</sup> *Sci. Am.*, **128** (1923), 224.



method differs from the preceding methods in that the precipitation depends upon the ease of electrically charging the suspensoid particles, and this is a function of the nature, temperature, and pressure of the gas as well as the electrical properties of the suspensoid "particles" themselves. Once the "particles" are charged, their removal from the gas follows a law like that of Stokes, where the mass of the particle is replaced by a quantity measuring the electrical charge.<sup>6</sup>

Our modern view of matter postulates that, in the metals, the electrons are "free" in the electric field, for they immediately attain a very high velocity when the field, though very weak, is applied. Electrical precipitation in metals thus consists of the motion and the accumulation of electrons. Places of difference of potential in metals mean simply places of different concentration of electrons. In electrolytes, comparatively intense ionization exists in the "free" state, and these "ions" are charged atoms, radicals, molecules, or aggregates of these. In dielectric solids, liquids, and in all gases no considerable number of "free" ions exist. Under these conditions ions are produced with difficulty and at great commercial expense. It is for this reason that all commercial processes which require the existence of ions or active chemical radicals should always be produced with metals or electrolytes if this is possible. A corona can be produced in some oils, but the danger of arcing is great.<sup>7</sup> In gases at low pressures or at high temperatures, ions can be produced with comparative ease, and the whole volume of gas subjected to the electric field becomes a conductor. This condition means the production of a large electric current. There are,

<sup>6</sup> The kind of suspensoids which have been precipitated include sulfuric acid mists; potash; precious-metal dust; blast furnace dust; pyrites burners dust; lead smelter fumes; alumina calcining furnace gases; waste gases from sulfite liquor evaporators; gases from McDougall roasters, briquetting furnaces, and copper converters; bacteria. (Cleaning of air by D'Arsonval, Bordas and Touplam, *Compt. rend.*, **170** (1920), 636; *J. Ind. Hyg.*, **1** (1919), 323.) The process is used for cleaning air; deblooming oil; chemical analytical purposes; fractional precipitation of materials of different volatility; treating meat by precipitated smoke; fertilizer dust; zinc oxide; the reported cracking of heavy oils from petroleum; the formation and precipitation of oxides of nitrogen as a by-product in precipitating fertilizer dust, etc.

<sup>7</sup> PEEK: "Dielectric Phenomena in High Voltage Engineering."

however, certain conditions, such as air at atmospheric pressure, when the gas about the conductor can be ionized while the electric current is kept comparatively small. The problem of cleaning a gas by the electrical precipitation method, therefore, consists of: (1) producing a maximum amount of ionization in the gas with the minimum amount of electric current through the gas, (2) the electrical charging of the suspensoid "particles" by the gaseous ions, (3) the removal of the suspensoid "particles" from the gas, (4) their collection, and, in case precipitated matter is deposited on a conducting electrode, as a pipe or plate, (5) the rendering of this deposited matter a conductor.

In all forms of electrical precipitation the suspensoid is passed between an active and a collecting electrode, where it is subjected to the ionization produced by the electrical discharge from the active electrode. The suspensoid "particles" become charged by combining with the ions of the electrical discharge and are then carried to the collecting electrode by the action of the electric field which is maintained between the electrodes. In recent years the precipitation of suspensoids has been found to depend very largely upon the acidity, temperature, and humidity of the suspensoid gases and sometimes these are artificially changed so as to better the precipitation.

The field to which the processes of electrical precipitation apply is vastly wider in the theory and the patent specifications than in commercial practice, in that the latter requires that the collected suspensoid should pay for the application of the process. The phenomena are also so pyrotechnic in demonstrations that the novice in the field is likely to be too enthusiastic. Keeping the electrodes and the insulators clean is a very serious problem. Nevertheless, there are several hundred electrical precipitation installations in the world and, as the electrical apparatus is developed, the process will become much more widely used.<sup>8</sup>

#### THE UNIDIRECTIONAL CURRENT AND THE CONDENSED ELECTRIC FIELD METHODS OF PRECIPITATION

Theoretically, modern science has reached the conclusion that all precipitation of "particles," and, indeed, all sorting of matter,

<sup>8</sup> *J. Am. Inst. Elec. Eng.* (July, Sept., and Dec., 1922).

are electrical. The ancients discovered electricity when they rubbed amber and found that it would attract small bodies and dust "particles." Everyone that has operated electrostatic machines has found that they soon become covered with dust and dirt. But until the development of transformers and rectifiers, such as that of the synchronously rotated rectifier of Lemp,<sup>9</sup> no one was able to produce any considerable ionization of gases and their contained "particles," so that the electrical precipitation of suspensoids from gases was not a commercial possibility. About the time of the development of the Wimshurst electrostatic machine, efforts to apply the process of electrical precipitation were made by Lodge and Walker, but lack of success was due to the small electrical current available. This work formed the basis for the basic patents on the use of unidirectional high-voltage currents for electrical precipitation.<sup>10</sup> The beginning of the present commercial application of the electrical method for the cleaning of gases was made by F. G. Cottrell.<sup>11</sup>

Many physicists during the nineteenth century had studied the wonderful figures that electrical discharges produce in dust surfaces, and phenomena of this kind were taken advantage of for the separation of ore particles, such as crushed silica from metalliferous gold. The electrical apparatus for this work is essentially that used in the electrical precipitation of suspensoids from gases.<sup>12</sup>

Electrical precipitators are of two types as regards (1) the direction of flow of the suspensoid, and (2) the direction of the electrodes. For purposes of symmetry, the electrodes are placed in a vertical position. In most instances the suspensoid flows along the electrodes. Rathbun has patented the use of "screens" for the passive electrode, the suspensoid thus easily flowing through the treaters with a minimum reduction of the draft.<sup>13</sup>

<sup>9</sup> U. S. patents 774090 and 774138 granted in 1904.

<sup>10</sup> WALKER: English patent Aug. 9, 1884, and U. S. patent 342548.

<sup>11</sup> U. S. patent 895729. For an account of his own work and that of others, see COTTRELL, F. G.: Problems in smoke fume and dust abatement, *Smithsonian Inst. Report*, 1913. For an excellent description of electrical precipitation apparatus and problems, see *Chem. Met. Eng.* (Jan. 15, 1919) and HORNE: *J. Am. Inst. Elec. Eng.* (July, 1922)

<sup>12</sup> See U. S. patents 685508 Dolbear, 805694 Wynne, 796011 Huff, 801380 Huff, 796012 Pickard, 859998 Wentworth.

<sup>13</sup> *J. Am. Inst. Elec. Eng.* (Sept., 1922).

For many years physicists have been developing the properties and the laws of electrical discharges between points and plates in gases, while at the same time electrical engineers have been deriving the expressions that describe the "corona" discharge which takes place from high-voltage transmission. As the "active" or "discharge" electrode used in electrical precipitators usually consists of wires, chains, or rods with sharp or serrated edges, the electrical discharge is frequently called a "corona," because it appears as a "halo" or "corona"<sup>14</sup> of light about the active electrode. The passive electrode is designed so that there is a minimum amount of electrical discharge taking place from it and so that it will serve for the deposition of the fume, dust, mist, or smoke which is being removed from the gas. The problem of the electrical engineer is to reduce the corona discharge to a minimum, while the problem of the electrical precipitation engineer is to produce a maximum of corona discharge and to see that this discharge remains uniformly distributed between the active and the collecting electrodes.<sup>15</sup>

The current  $I$  flowing in a precipitator can be roughly represented by an equation of the following type:

$$I = A_s \frac{(V - V_x)V}{V_y - V} = A_s xyf(V) \quad (4)$$

In one case the writer has found that there is about one ion per 2,800,000,000,000 air molecules for an electrical treater, taking a maximum ionization current.<sup>16</sup>

$V$  represents the voltage at which the current  $I$  flows;  $A_s$  is a quantity depending on the nature of the suspensoid;  $V_x$  is the voltage at which corona starts; and  $V_y$  is the voltage of spark-over. If the precipitator is connected to a smelter furnace,  $A_s$ ,  $V_x$ , and  $V_y$  may change suddenly and vary between wide limits. If sulfuric acid mist from heating kettles is being precipitated, these quantities may remain fairly constant. If conditions were constant and uniform,  $A_s$ ,  $V_x$ , and  $V_y$  can be evaluated in terms of the properties of the gas, ions, and the suspensoid "particles." (For a gas under uniform conditions, Warburg gives an equation  $I = a(V - V_x)V$ , where  $V_x$  is a constant.)

<sup>14</sup> Corona discharge, *Bull.* 114, Univ. of Ill., Urbana, Ill.

<sup>15</sup> For a review of this work, see articles in the *Phil. Mag.* and *Phys. Rev.*

<sup>16</sup> *J. Am. Inst. Elec. Eng.* (June, 1913).



Neglecting space charges, the potential gradient  $E_r$  is, approximately,

$$E_r = \frac{V}{r \log_e \frac{R}{a}} \quad (5)$$

It follows from considerations of these equations that the mobility of ions causing a space charge must be small or zero, *i.e.*, deposited on the passive electrode.<sup>17</sup>

The electric capacity of a pipe treater of unit length is

$$C = \frac{7.354(10)^{-3}K}{\log_{10} \frac{R}{r}}$$

The above is in microfarads if the length is in terms of 1,000 ft. For air,  $K$  is unity. To bring  $C$  to electrons, multiply by  $1.9(10)^{16}$ .  $R$  is the radius of the pipe and  $r$  is the "radius" of the corona.

It is now generally considered that the proper ionization of the gas is not the most serious problem in removing fumes from gases at high temperatures. In the case of poorly conducting fumes, such as zinc oxide, one of the problems consists in getting the gas ions to combine with the small zinc oxide crystals. Once the poorly conducting fume "particle" is charged, it is carried to the collecting electrode, and it may then be very difficult to remove its electrical charge. Under these conditions the collected fume material may not only act as an insulator to reduce the ionization current, but it may hold an electrical charge itself which will prevent other charged particles from being carried to the collecting electrode. In order to prevent the above conditions, the gas which is being treated is "conditioned" by the addition of steam, acid, or other material which will either make the suspensoid "particles" more easily charged, or make their precipitated deposit a better conductor, or function in both of these ways at the same time. Wolcott<sup>18</sup> supplies

<sup>17</sup> See STRONG, W. W.: Elektrische Fällung, *Ann. Phys.* (Oct., 1915); Some theoretical aspects of electrical fume precipitation, *Trans. Am. Electrochem. Soc.*, **31** (1917) 415.

<sup>18</sup> WOLCOTT, E. R.: *Phys. Rev.* (Oct., 1918); also U. S. patents 1329818, 1383586 and 1416769.

water to humidify the hot fume gases so as to prevent the accumulation of electric charge on the precipitated material. Witte<sup>19</sup> adds clay, sand, earth, etc. to improve precipitation.

According to equation (5), for an electrical precipitation pipe with air, the corona starts when there are about 1,700,000,000 electrons per square centimeter of active electrode, or the voltage gradient is about 30,000 volts per centimeter. In the case of a pipe 6 in. in diameter, the electric gradient at the pipe is only about 1,000 volts when the corona starts. If the precipitate is a poor conductor, an electric charge accumulates near the pipe and greatly weakens the electric field at its weakest point. Like the weakest link in a chain, electrical precipitation cannot be any better than it is at its place of minimum efficiency. Precipitation engineers have, therefore, stressed this problem of insulating fume forming on the collecting electrodes. The failure of methods of mechanical cleaning of the collecting electrode, such as shaking and scraping, has led to the ultimate resource of adding something to the fumes so that the precipitate becomes a fairly good conductor. The fundamental reason is that the electric force which causes precipitation is by nature a local force subjected to local electric charges, whereas there is no analogy of this kind in the case of the mechanical forces. Although the fume ions move slowly—about 2 cm. per second, according to Eschholz<sup>20</sup>—the main disturbance to the electric field is due to the precipitate.

A current of an ampere through a precipitation treater means the flow of about  $54 \times 10^{15}$  ions per alternation of 60-cycle current. About 300,000,000 ions are required per foot to change the potential a volt between the electrodes. These are approximate values. Only a few ions ever combine with the suspensoid "particles."

Let us assume that the precipitator consists of wires of radius  $a$  within pipes of radius  $R$ . Let the corona have a radius  $r_c$  and let the fall of potential across the corona be  $V_c$  and the electric field strength  $E_r$ . Let equilibrium conditions exist with  $N$  ions formed per unit time, and assume that each ion carries a charge  $e$ .

<sup>19</sup> U. S. patent 1446778.

<sup>20</sup> *Proc. Am. Inst. Mining Mech. Eng.*, **60** (1919), 243.

In the electrical process of Lodge, Walker, Cottrell, etc., the wire or active electrode is kept negative, so that the corona is a region where ions are produced and the positive ions are constantly flowing towards the active electrode. The negative ions flow from the corona to the passive electrode. The number and kind of ions in any region are the measure of the space charge in that region. Naturally, a dense non-conducting suspensoid causes the electric charges to pile up, distorts the electric field tremendously, and causes sparking and arcing. In the condensed electric field method of electrical precipitation,<sup>21</sup> a dielectric is placed between the active and the passive electrodes so that the intensity of the ionization, the extent of the corona, and the intensity of the electric field can be greatly increased. This process is especially suited for dielectric suspensoids and small pipes, and smaller voltages can be used, whereas the unidirectional current method is not suited for operation at low voltages. The unidirectional method of electrical precipitation always requires a rectifier and this cannot be as simple and compact as the condensed electric field method.

In the ionization about the active electrode we may assume the number of positive ions  $\frac{1}{2}N^+$  to be equal to the number of the negative ions  $\frac{1}{2}N^-$ . Let the corresponding mobilities of the ions be  $K^+$  and  $K^-$ ; the corresponding velocities  $V^+$  and  $V^-$ ; the corresponding periods or lengths of life be  $T^+$  and  $T^-$ ; the tracks to the electrodes  $C^+$  and  $C^-$ ; and the "average effective" electric fields which cause these ions to be precipitated to the electrodes,  $E^+$  and  $E^-$ .

$$\text{Then} \quad I = Ne = \frac{1}{2}(N^+ + N^-)e = A_s \frac{(V - V_x)V}{V_y - V} \quad (6)$$

$N$  varies roughly as  $V^2$ . The periods of the ions are

$$T^+ = \frac{r_c - a}{K^+E^+} = T^- = \frac{R - r_c}{K^-E^-} \quad (7)$$

In case the active electrode is kept negative, the negative ions act as the precipitators. Y. Niwa<sup>22</sup> claims that if there are  $S$

<sup>21</sup> STRONG, W. W.: U. S. patents 1070536, 1096765, 1325124, etc.

<sup>22</sup> *Inst. Elec. Eng.*, Japan (1922), no. 402, 47-54.

suspensoid "particles" with a velocity  $v_s$ , and mobility  $K_s$ , then the charge on the "particles" is

$$\frac{1/4 N^- V^-}{S v_s} = x e \quad (8)$$

For practical purposes these relations should be determined at high temperatures. One reason for not defining the above terms more exactly is due to the great variability in the conditions. For the above,  $v_s = K_s E^-$ . Pascal<sup>23</sup> found the following values for sulfuric acid "particles."

Temperature, deg. C. ....	24	32	52	55
$K_s (\times 10^{-4})$ .....	2.4	4.9	13.6	15.1

The writer has found that there is a very close connection between increase in the pressure of the gas in a closed electrical treater and the precipitation force. As an example of the use of this relationship, it was found that a unidirectional corona current within a small pipe was very small, but that, by using the method of the condensed electric field, the corona could be made to increase the gas pressure very considerably. The term "precipitating force" expresses the cleaning versus the voltage, fume velocity, temperature, etc. of a particular treater, in the form of a curve, and any change in this curve is caused by abnormal conditions in the treater. In the case of a centrifuge the precipitating force depends upon the square of the speed of the rotation, and the precipitation-force curve would be plotted for a given kind of fume. In the measurement of the increase of the pressure  $p$  due to the ionization, care must be taken either to keep the temperature  $t$  constant or to measure  $p$  for a given length of time. An approximate equation of the corona pressure<sup>24</sup> is

$$p = \frac{A I t V}{B} - \frac{C V t}{B} = \frac{t V}{B} [A A_s x y f(V) - C] = F(V) \quad (9)$$

where  $B$  depends upon the volume,  $A$  is a constant, and  $C$  a constant. The writer has defined the "precipitating force"

<sup>23</sup> *Chimie & Industrie* (Sept., 1920).

<sup>24</sup> Corona pressure, *Bull.* 114, Univ. Ill. Eng. Exp. Sta., p. 87.



$P$ , or constant,<sup>25</sup> so that this term would include the local properties of the treater electrodes and suspensoid and thus permit  $P$  of one treater to be compared with that of another treater in the same way that centrifugal and gravity forces are compared.

If  $v_e$  is the velocity of the fume along the electrodes (or normal to the electrodes in the case of Rathbun's "screen" treater),

$$P = f\left(\frac{1}{v_e}\right) \frac{V_p K}{\log_e \frac{R}{r_c}} = F'(V), \quad (10)$$

where  $V_p$  is the voltage between the corona and the pipe. It must be remembered that equation (10) is employed simply because the relation between  $E_r$  and  $r$  (for voltages approaching  $V_y$ ) has not yet been experimentally determined for voltages such as 50,000 to 100,000. It is quite likely that  $E_r$  falls very low as  $r$  approaches  $R$ . Equations (9) and (10) support the view that  $p$  and  $P$  are closely related provided a sufficient number of variables which one encounters in practice are kept constant. Then

$$P = F''(p) \text{ and } p = F'''(P) \quad (11)$$

The elements of electrical precipitation include the ionization  $I$  of the suspensoid gases, the chargeability  $S_c$  of the suspensoid "particles" by the  $I$  ions,

$$S_c = f(N, V, S, V_p, \text{ etc.}) \quad (12)$$

the precipitation force, and the dechargeability of the precipitated suspensoid

$$S_d = f(S) \quad (13)$$

a function of the conductivity and physical character of  $S$ .

Experiments will undoubtedly simplify many of the above expressions. For instance, the "life" of the suspensoid "particle" will enter (9), (10), and (11). The writer has used the relation

$$T^- = \frac{1}{4v_e P} (R^2 - r_c^2) \quad (14)$$

where  $T^-$  is an "average." The tracks of the suspensoid "particles" are functions of  $P$

$$C^- = f(P, V_e, \text{ etc.}) \quad (15)$$

<sup>25</sup> *Trans. Am. Electrochem. Soc.*, **31** (1917), 427.

The term "efficiency" may be defined in various ways. The efficiency of charging would be  $\frac{N^-}{S}$ . The efficiency of energy consumption may be taken as the ratio of the energy actually employed to overcome the frictional forces  $Ef$  as given by the law of Stokes<sup>26</sup>

$$Ef = B \int_{r=a}^{r=R} r dr f \left( \frac{E}{r \log \frac{R}{a}} \right) - C \int_{r=a}^{r=R} r^2 dr f \left( \frac{E}{r \log \frac{R}{a}} \right) \quad (16)$$

and the total energy  $E_t$  applied to the treater. Under such conditions the efficiency would depend upon the density and nature of  $S$ . Ordinarily, the ratio of the "amount" or "opacity" of  $S$  entering and leaving the treater is called the "percentage of precipitation."

The range in the size, cost, and the electrical technique of electrical precipitators is very great. The earlier precipitators and the large installations make use of a unidirectional corona current. Voltages as high as 250,000 have been used, though during the past few years the trend has been towards voltages below 60,000. Precipitators involving costs as high as a million dollars have been installed for cleaning the fumes from large smelters. In the largest treaters the total length of electrodes, if placed end to end, would be hundreds of miles. In large installations the electrical equipment appears to operate better if made up of 5- to 15-kv.a. units.

On the other hand, small electrical precipitators operating on the condensed electric field principle and using dry batteries have been developed so that the initial cost is as low as \$8. These use corona discharges at as low as a few thousand volts. They can be used as fume masks, for cleaning gases which enter indicating and recording instruments, for determining the dust and the bacteria content of gases, for collecting suspensoids in analytical chemical processes, and for the precipitation, on even the largest scale, of suspensoids that form an insulating deposit on the collecting electrode. The use of the alternating condensed electric field type of precipitator promises to develop under conditions where the problems of exposed high-voltage apparatus,

<sup>26</sup> STRONG: *Proc. Am. Inst. Elec. Eng.* (Feb. 19, 1915), 235.

such as mechanical rectifiers, is to be avoided. The smallest of these precipitators weighs only a few pounds and is especially suited for laboratory and lecture work.

For treating large volumes of gases, the electrical centrifuge of McGee and Nesbit promises to open a new field, in that this apparatus cleans gases at high velocities. The apparatus is comparatively small in volume and has succeeded in clearing gases moving at the velocity of 40 ft. a second. In this way the problems of the large electrical treater, such as the uniform distribution of the fume gases between the various electrodes, is immediately solved.

The cost and the size of large precipitators have been given in formulas, but the constants of the formula are not given. Anderson<sup>27</sup> gives

$$x = \frac{a[\log b - \log (c \log d)]}{\log d}$$

where  $x$  is the maximum size of the precipitator,  $a$  is the gas volume,  $b$  is a function of the cost of a unit size precipitator,  $c$  is the value of the solids carried, and  $d$  is a function of the specific precipitation ratio of the fume.

The process of electrical precipitation will probably be greatly advanced in the near future. The great problem in the past has been the experimental work which has been required for new installations. Suspensoids differ so widely that the process has not been standardized. It may be possible that some compact form of apparatus, like the electric centrifuge, will make standardization possible. In the meantime large installations will continue to require considerable preliminary investigation before their erection.

## SUMMARY

1. The present section deals with the fundamental relations and laws which govern the removal of suspensoids from gases. A complete research should be made as to the numerical application of these laws for known and reproducible conditions, which include commercial applications within its range. For instance,

<sup>27</sup> *Chem. Met. Eng.*, **26** (1922), 151

few data are available on the effect of change of temperature on intense ionization currents. Naturally, the field engineers want data on their particular problems, but, when they have several variables changing together, their results are extremely difficult of interpretation. This research should include electrical precipitation as one of its fields. An example of this kind of work in a limited field is given by Peek's "Dielectric Phenomena in High Voltage Engineering." There is no field as well suited for giving the student the modern ionic concept of electrical phenomena as that of ionization currents and visible particle precipitation between wires and pipes.

2. In precipitation the mechanical forces are independent of the gas and the suspensoid as well as the temperature. In this type of precipitation it is the "forces of friction" which involve the properties of the medium. The nature of the medium determines the velocity of the precipitation. Electrical precipitation is special in that the ionization of the gas affects the electric field, the precipitating force itself. One of the most serious of precipitation problems is that of preventing the precipitate from decreasing the cleaning effect.

3. The mechanical construction of treaters, the regulation of draft, the type of insulation, the design of transformers, and the use of rectifiers or kenetrons have become largely matters of technique for large installations and require the review of the literature and the aid of precipitation experience.

4. The processes of precipitation have been classified and briefly described by equations. The unidirectional current, the condensed electric field, the electrical centrifugal, and the screen electrode types of electrical precipitation have been described. Ultimately, the whole process of precipitation will be accurately represented by relations of which the law of Stokes will be prominent.



## CHAPTER XXIV

# THE COLLOIDAL CHEMISTRY OF SILICA AND ITS DERIVATIVES

By

WILLIAM STERICKER

SILICATES OF SODA

When the colloidal chemistry of silica is spoken of, perhaps the first thing that comes to mind is silica gel. But it must be remembered that this is derived from silicates of soda,<sup>1</sup> substances the colloidal properties of which are evident from the moment of preparation. Since these silicates are little known<sup>2</sup> and the methods by which they are converted to silica gel affect the properties of the gel, they will be considered first.

When soda ash is fused with more than one equivalent of silica, a glass results. When there is only slightly more than one equivalent of silica, the glass may partially crystallize to sodium metasilicate. These fusions dissolve slowly in cold water and readily in hot water. As the proportion of silica increases, these glasses dissolve with increasing difficulty. When the ratio is  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ , the glass dissolves to some extent, but it is difficult to complete the solution. By the time  $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$  is reached, not only are special methods necessary, but the dissolution is very slow. Slightly above this ratio, the solubility becomes so slight that the glass is considered insoluble.<sup>3</sup>

**Solution.**—The silicates of soda which are used commercially are not definite compounds. For that reason the different va-

<sup>1</sup> This term is used to indicate the variable systems of sodium oxide and silica, with or without water, which are the commercial products. The writer reserves the term sodium silicates for definite compounds.

<sup>2</sup> This is startling in view of the fact that among sodium compounds the production of silicates of soda is third in quantity and value. The production in 1919 was 336,093 tons, valued at \$7,057,953.

<sup>3</sup> COBB: *J. Soc. Chem. Ind.*, **29** (1910), 399.

rieties are best designated by the ratio of sodium oxide to silica. The kind of silicate of soda which finds the greatest market in this country is a solution of approximately  $\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$ . This is made by running the molten fusion of sand and soda ash into a large revolving drum partially filled with water. The silicate is broken up into a spongy mass called "cullet." Apparently, there is some hydration or swelling at the same time, for this material dissolves much more readily and rapidly than glass broken or ground up to the same size or even smaller.<sup>4</sup> The difference is more strikingly shown by the scheme used in the analysis of silicate of soda glasses.<sup>5</sup> If the glass is ground and then heated or boiled with water, there is a large insoluble residue and only a small portion of the alkali will go into solution. If, however, the ground glass is first exposed to an atmosphere of steam, it will become hydrated and will then dissolve readily in warm water.

**Viscosity.**—The solutions that result have the characteristics of emulsoid or lyophilic sols. This is, perhaps, most strikingly shown by the viscosity changes which are typical of that type of colloids. The viscosity increases only slightly with the concentration when the latter is low, but increases rapidly after the concentration reaches a critical value. The slope of these curves is dependent on the ratio of sodium oxide to silica. When this is in the neighborhood of 1 to 4, the change in direction is very abrupt. As the silica becomes proportionately less, the change in direction becomes more gradual. Thus, a change in concentration of 1 per cent in a solution of  $\text{Na}_2\text{O} \cdot 3.9\text{SiO}_2$  increases the viscosity from 375 to 7,025 centipoises, while with  $\text{NaO} \cdot 2\text{SiO}_2$  about 8 per cent change is necessary for the same increase. The cause of this difference may be either the peptization of the colloidal material or the formation of a crystalline compound at the expense of the colloidal constituents. Both of the processes may take place. This rate of change of viscosity is important from the technical standpoint, since it measures the rate of set when the silicate is used as an adhesive.

<sup>4</sup> The commercial method of solution in England is somewhat different, but a similar hydration effect has been noticed.

<sup>5</sup> This method was developed in the laboratories of the Philadelphia Quartz Company, by J. G. Vail.

The viscosity at a given concentration passes through a minimum when the ratio is between 1:2 and 1:3. This is shown in Table I.

TABLE I.—EFFECT OF THE SODA-SILICA RATIO ON VISCOSITY

Concentration of total solids, per cent	Viscosity in centipoises				
	Na <sub>2</sub> O· 3.9SiO <sub>2</sub>	Na <sub>2</sub> O· 3.4SiO <sub>2</sub>	Na <sub>2</sub> O· 2.4SiO <sub>2</sub>	Na <sub>2</sub> O· 2.1SiO <sub>2</sub>	Na <sub>2</sub> O· 1.7SiO <sub>2</sub>
26	20	19	14	18	17
28	29	22	17	21	21
30	50	26	20	23	25
32	233	36	23	27	30
34	>7,000	59	28	25	40

**Elasticity.**—The gels formed by concentrating the more silicious silicates are very elastic. If they are formed into balls and dropped about 40 ft., they will rebound at least two-thirds of that height. Yet these gels will flow out and take the shape of the container they are placed in, so that they must be classed as fluids. In fact, if a point is drawn out on the surface, it will disappear in a short time, indicating that the gel does not have an appreciable yield value. Apparently, here are elastic solids which are liquids. These elastic gels are also friable, crushing under light pressure between the fingers. When this extremely small compressive strength is considered, the great elasticity is even more remarkable.

**Ultramicroscopic Examination.**—When solutions of glue are examined under the ultramicroscope, it is hard to distinguish any particles. Presumably, this is due to the high degree of hydration which makes the particles relatively large and of nearly the same refractive index as water. This is not true of a solution of Na<sub>2</sub>O·3.3SiO<sub>2</sub>. At concentrations of 37 and 18.5 per cent, there are myriads of tiny particles clearly distinguishable. This indicates that at these dilutions, at least, the colloidal portion is not greatly hydrated.

**Conductivity.**—Kohlrausch studied the conductivity of silicates of soda up to  $\text{Na}_2\text{O} \cdot 3.4\text{SiO}_2$ . He found<sup>6</sup> that they conducted well in dilute solution, but very poorly when concentrated. In fact, *sodium metasilicate in dilute solution was a better conductor than any other salt at equivalent concentration*. Very little was said about the experiments in concentrated solutions.

**Cataphoresis.**—When such solutions of the more silicious silicates are subjected to a potential difference, there is a brisk evolution of gas at the negative electrode and a much smaller amount at the positive one. The evolution of gas soon ceases. Cataphoresis proceeds slowly, building up a vitreous layer on the anode, showing that the colloidal particles in the solution are negative.

If a mercury cathode is used with a dilute solution, the ratio of silica to sodium oxide may be increased.<sup>7</sup> As the alkali is removed, the current decreases. With 1.5 per cent of a silicate of unknown ratio (probably  $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ ), the current dropped from 0.55 to 0.08 amp. in 2 hours, with 8 volts. The sol was neutral to litmus and would gelatinize in about 4 weeks on standing. The addition of acids hastened the gelation. A 6 per cent solution became neutral after about 2 hours. These sols gelled so rapidly that the waves formed by stirring set in their shape.

**Deflocculating Effects.** *Clay Casting.*—When small amounts of silicate solutions are added to suspensions of finely ground quartz, clay, or alkaline earth carbonates, the solid is deflocculated. In casting clay, as in the manufacture of sanitary ware and glass pots, about 0.1 per cent each of  $\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$  and sodium carbonate are added to the filter cake. This contains about 20 per cent of water as a rule and is a stiff, plastic mass. As the alkaline salts are worked in, the mixture becomes more and more fluid until finally it can be pumped readily through 1-in. pipes. This fluid "slip" will run into plaster molds, which absorb water and flocculate the clay.<sup>8</sup> The setting action is sufficient to permit the removal of the inner portion of the mold after 2 hours. The outer portion is removed after 24 hours.

<sup>6</sup> *Ann. Phys. Chem.*, **47** (2), (1892), 756; *Z. physik. Chem.*, **12** (1893), 773. The second article gives more complete data.

<sup>8</sup> KROGER: *Kolloid-Z.*, **30** (1922), 16.

<sup>7</sup> FOERSTER: *Chem. Ind.*, **28** (1905), 733.



It is necessary to use a silicate or some similar agent in the electrical casting of clay.<sup>9</sup> An undeflocculated slip containing 30 per cent of a mixture of clay, flint, and feldspar is about as stiff as can be handled. When this is deposited in a mold by electricity, a creamy layer forms. The addition of 0.1 to 0.3 per cent of sodium silicate causes some precipitation of the feldspar and flint. When more of the mixture is added, the precipitated material is again taken up. It then requires 60 per cent solids to give the same fluidity as was obtained with 30 before. This slip gives a solid, compact deposit when subjected to a current.

*Clay Purification.*—The decrease in viscosity produced by silicate is also used in the purification of clay.<sup>10</sup> The coarse particles settle out more readily and, in addition, many impurities are not deflocculated as the clay is. For example, the rate at which particles of pyrites settle in a solution of sodium silicate is greater than in pure water, but that of clay particles is much less.<sup>11</sup>

Schurecht, working with Georgia kaolin and  $\text{Na}_2\text{O} \cdot 3.1\text{SiO}_2$ , found that about 0.25 per cent of the weight of the clay gave the minimum viscosity. The relation of the silicate to the clay is more important than that to water. At the point of minimum viscosity, 58 per cent more clay can be treated before a set standard fluidity is reached. The values for sodium hydroxide and carbonate are 54 and 50 per cent respectively. In addition, the silicate produces a greater drop and is not likely to cause reflocculation with an excess. Apparently the finer grains pack together more than the undeflocculated ones, for the porosity decreases and the dry density increases. Between 0.25 and 2 per cent, there is less shrinkage on drying than with either sodium hydroxide or carbonate. The modulus of rupture increases from less than 300 lb. to a maximum of 800 lb. with 2 per cent  $\text{Na}_2\text{O} \cdot 3.1\text{SiO}_2$ . Caustic soda is the only reagent which is more effective.

Silicates of soda also deflocculate other materials, such as quartz, alkaline carbonates, barium sulfate, and mica.

<sup>9</sup> KLEEMAN: *Phys. Rev.*, **20** (1922), 272.

<sup>10</sup> BLEININGER: *Bur. Standards Tech. Paper* **51** (1915); SCHURECHT: *Bur. Mines Tech. Paper* **281** (1922).

<sup>11</sup> KOHL: *Ber. deut. keram. Ges.*, **3** (1922), 64.

It has been proposed to subject the deflocculated clay to an electrical potential difference in order to remove its impurities.<sup>12</sup> Kohl,<sup>13</sup> however, did not secure any purification by the electrical treatment, so that it does not seem necessary.

Rohland<sup>14</sup> concluded that the undissociated alkali silicates in the colloidal condition are active ingredients in the solutions. It is certain that silicates give results which cannot be obtained with other alkaline salts or with alkalis. There is some dispute as to the best time to add the silicate and, when used, the carbonate. Generally, the salts are dissolved in water and blunged in. Shory<sup>15</sup> claims that it is best to do this as early as possible.

*Flotation.*—This deflocculating effect of sodium silicates on silicious and argillaceous materials finds application in flotation. It has been found that the greater the degree of dispersion of the constituents of the gangue, the less they are carried into the froth.<sup>16</sup> The silicate solutions have a wider range through which they act than most deflocculating agents. They also flocculate certain kinds of ores, notably copper sulfides, thereby rendering them more easily floated and stabilizing the froth. Three to four pounds are used per ton of ore.

Silicate has been applied to some extent in differential flotation. It seems especially effective with mixed lead and zinc sulfide ores. Each ore seems to be a distinct problem, so that it is hard to summarize the results. Sodium silicate alone will not deflocculate blende but in a mixture with sodium oleate it will. This fact is used to separate galena, which remains flocculated, from the blende. If the latter is light-colored, it can be reflocculated merely by diluting the liquid, but not if it is dark.<sup>17</sup> In a series of tests on Idaho ores containing galena and sphalerite, it was found that sodium silicate increased the recovery of zinc.<sup>18</sup>

<sup>12</sup> SCHWERIN: Brit. Pat.; cf. "Second Report on Colloid Chemistry," p. 49.

<sup>13</sup> *Loc. cit.*

<sup>14</sup> *Kolloid-Z.*, **15** (1914), 158.

<sup>15</sup> *J. Am. Ceramic Soc.*, **3** (1920), 286.

<sup>16</sup> SULMAN: *Bull. Inst. Mining Met.*, **29** (1920), 49.

<sup>17</sup> EDSEER: "Fourth Report on Colloid Chemistry," 1922, pp. 321-322.

<sup>18</sup> WRIGHT, PARMELEE, and NORTON: *Bur. Mines Bull.* **205** (1921).

Borchardt has applied sodium silicate to other methods of ore concentration as well as to flotation.<sup>19</sup> The gangue may be thoroughly deflocculated and removed by decantation from the settled concentrate. The amount of silicate used varies from 0.5 to 5 lb. per ton of dry ore. Acid ores must be neutralized and excessive electrolytes must be washed out before this method will work. The concentrate may then be filtered or subjected to hydraulic classification or to flotation.

**Action of Salts.** *Sodium Chloride.*—When salts are added to solutions of silicate of soda, the results are due to the combined effects of a number of different factors. The simplest cases are those of sodium salts, for then no complications due to changing bases arise. When a concentrated solution of sodium chloride is added to a silicate of soda solution, a gelatinous precipitate is formed which tends to become hard and granular. If the addition of brine is continued, this precipitate is again peptized.

During the World War, when it was hard to ship silicate, Malcomson<sup>20</sup> developed a method to extend the volume of the silicate solution without changing its viscosity. By properly adjusting the concentration of brine, he was able to mix 1 volume of it with 4 of the silicate solution. There is a contraction on mixing, so that the net increase in volume is only about 21 per cent. This method has not been adopted anywhere. It was found that the adhesive properties of the extended solution were not as good as those of the original, and the cost of mixing usually was greater than that of the silicate replaced.

A study of this reaction revealed that it was not simply a case of changing the quantity of water present as active solvent, although this is undoubtedly a factor. The charge on the particles was not reversed, but the hydroxyl ion concentration was changed. The indications were that the pH value passed a minimum at the concentration of brine which restored the original viscosity. The addition of salt of course decreased the hydrolysis and dissociation of the silicates. In addition, Glixelli<sup>21</sup> found that sodium chloride and other sodium salts developed the acidity of the silica sols.

<sup>19</sup> U. S. Pats. 1446375-8; 1448514-5 (1923).

<sup>20</sup> *J. Ind. Eng. Chem.*, **12** (1920), 174.

<sup>21</sup> *Compt.-rend.*, **176** (1923), 1714.

Manson<sup>22</sup> found cases where the concentration of brine required in Malcomson's method was inversely proportional to the excess of silica over that required for  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ . Mylius<sup>23</sup> had found that when sodium chloride is added to silicate solutions and the mixture heated, a precipitate forms only when the ratio exceeds 1:2. However, Manson's relationship is not generally true, nor is there a relationship to the total silica. Roughly, the concentration of brine required is inversely proportional to the Baumé gravity of the silicate.

*Ferric Chloride.*—A number of investigators have worked with ferric chloride and sodium metasilicate. When 0.01 molar solutions of these two are mixed in equivalent proportions, a precipitate containing about two-thirds of the total iron and silica separates from an acid solution containing the rest of these materials. Even then the iron and silica are not equivalent, for there is an 8 per cent excess of iron in the precipitate and a corresponding excess of silica in the filtrate. A further precipitation may be obtained by heating or by adding sodium chloride. A greater proportion of the residual iron and silica are thrown out by the former method but in either case there is a great excess of iron. If the original filtrate is neutralized with alkali, turbidity appears first, then a precipitate. The solution clears at the neutral point. In order to get an alkaline reaction with either litmus or tumeric, it is necessary to add considerably more alkali. The amount is greater when the precipitate remains in the solution than when it is filtered off. When the precipitate remains, the alkaline solution slowly becomes neutral, so more alkali can be added. The precipitate itself, when freshly made, is soluble in cold, dilute hydrochloric acid but after standing it is only partially soluble.<sup>24</sup>

When the proportions are as  $\text{FeCl}_3$  is to  $\text{Na}_2\text{SiO}_3$ , no precipitate forms, but the clear acid solution acts like the filtrate in the former case, except that the neutral zone is greater. When  $\text{FeCl}_3$  is mixed with  $3\text{Na}_2\text{SiO}_3$ , 99.8 per cent of the iron is precipitated but only 44 per cent of the silica. The filtrate is alkaline.

<sup>22</sup> Private communication.

<sup>23</sup> *Speersaal*, **41** (1908), 140.

<sup>24</sup> JORDIS and HENNIS: *Z. angew. Chem.*, **19**, (1906), 1697.



When more complex silicate solutions are used, the reactions are still more complicated.

*Other Chlorides.*—The effect of zinc and cadmium chlorides on concentrated solutions of  $\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$  are much the same as those of sodium chloride, except that much smaller amounts are required. Another difference is that a permanent precipitate forms in a shorter time after the treatment.

*Aluminum Sulfate.*—The more silicious of the commercial solutions of the silicates of soda are used in various industries in connection with aluminum sulfate. The two solutions, when mixed, yield a precipitate of variable composition. It comes out of dilute solutions in fine gelatinous flakes. Gottwald found that the precipitate contained alkali compounds and aluminum silicate.<sup>25</sup> The reaction reaches equilibrium while the solution still contains aluminum and silica.

*Paper Sizing.*—This reaction is used in the “mineral sizing” of paper. Apparently, the gelatinous precipitate is adsorbed by the paper stock, for it is carried into the sheet of paper. In addition, it holds some of the very fine fibers which otherwise go through the screens into the “white” or “back” water. The sheet has a smoother, harder finish than it otherwise would have. The hydration of the fibers is increased. The silicate precipitate sizes for printing ink, which has an oil base, but its only advantage for aqueous inks is the hydration and a possible increased retention of the rosin size.<sup>26</sup>

*Other Sulfates.*—In general, the precipitate contains a greater proportion of the silica when metallic sulfates are mixed with very dilute solutions of sodium metasilicate than when ferric chloride is used. The metallic ion is entirely precipitated from ferrous, copper, or nickel sulfate in 0.01 molar solution unless it is in excess of the silicate ion.

*Silicate Gardens.*—When concentrated solutions of metallic salts come into contact with concentrated solutions of  $\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$  and other silicious silicates, semi-permeable membranes are formed. These membranes are very strong when they are formed in Morse and Frazer cells. For this reason they are valuable in the study of osmotic pressures. The formation of

<sup>25</sup> Dissertation, Erlangen (1913), through *Chem. Abs.*, **10**, (1916), 726.

<sup>26</sup> Cf. VAIL: *Chem. Met. Eng.*, **25** (1921), 823.

these membranes is the basis of a pretty experiment. When crystals of various metallic salts are dropped into an 18 per cent solution of  $\text{Na}_2\text{O} \cdot 3.3\text{SiO}_2$ , plant-like structures grow up from them.<sup>27</sup> Colored salts give colored shoots. The forms which the membranes take depend on the salt used. For example, a thick fungoid growth results from nickel salts and fine, hair-like shoots from cadmium salts.

### SILICA SOLS

Graham<sup>28</sup> prepared silicic acid sols by the action of hydrochloric acid on some sodium silicate solutions. These he dialyzed for 6 to 8 days, securing sols containing up to 4 per cent of silica. They were coagulated by carbon dioxide, but could be concentrated up to 16 per cent silica in its absence. Later investigators were not able to secure as high concentrations.

Finally, Jordis and his students, especially Kanter, studied the pure sols extensively. They acidified pure sodium metasilicate made from dialyzed silica, and dialyzed it. Chlorides disappeared in 8 to 10 days, but the flame test showed sodium was still present. It did not disappear for 3 to 4 weeks. A pure sol obtained at the end of 6 weeks was stable at concentrations below 1.5 per cent but coagulated suddenly at that point. If a drop of either alkali or hydrochloric acid was added, the sol could be concentrated to 4 per cent. When the pure sol was dialyzed in a special apparatus<sup>29</sup> for 8 weeks, plates of silica separated from a sol containing 0.6 per cent silica. An attempt to prepare a sol from ethyl orthosilicate was no more successful. A sol containing 0.1 per cent silica was obtained, but it contained organic matter. From these experiments and others Jordis was led to the conclusion that pure colloidal silica sols did not exist but that silica was always stabilized by some "sol-former" which might be acid, alkali, or organic material.

Further light on this subject was given by Mylius and Groschuff.<sup>30</sup> They found that metasilicic acid actually exists when

<sup>27</sup> DOLLFUS: *Compt. rend.*, **143** (1906), 1148; Ross: *Proc. Roy. Soc. N. S. Wales*, **44** (1910), 583; through *J. Chem. Soc.*, **102**, II (1912), 49.

<sup>28</sup> *Phil. Trans.*, **151** (1861), 183; *J. Chem. Soc.*, **15** (1862), 216.

<sup>29</sup> JORDIS: *Z. Electrochem.*, **8** (1902), 677.

<sup>30</sup> *Ber.*, **38** (1905), 116.

freshly prepared. It will pass through semi-permeable membranes. Polymerization commences almost immediately and the molecular weight increases for several weeks.

Silica sols may be formed by disintegration as well as by agglomeration. Lenher and his students<sup>31</sup> found that by grinding Ottawa sand for 350 hours or more a portion of it was reduced in size until it formed a stable suspension in water. Most of the particles were less than 0.004 mm. in diameter. The sol contained 0.028 to 0.032 g. of silica per liter. It showed a pronounced Tyndall cone and the particles, in rapid Brownian movement, were visible under the ultramicroscope.

When this finely divided silica is heated with water it gelatinizes, and, eventually, part of it goes into solution. This action is aided by temperature and pressure. With an excess of water in a pressure bomb at 300 to 450°, gels containing 15 to 18 per cent of water are formed. A dialyzed gel made in the usual way and heated under the same conditions changed from 97.77 to 70 to 80 per cent water, showing that the equilibrium is not the same.

Alkalies aid in this action. It has been proposed to prepare silicate of soda by this method. The gelatinized silica dissolves in caustic soda at high temperatures and pressures. The source of silica was to be diatomaceous earth.<sup>32</sup> Other kinds of finely divided silica could be used. This method has been used in a few small installations but almost all silicate is made by the fusion of sand and soda ash. Both of the latter materials are much cheaper than those required in the wet process. In addition, the practical difficulties in handling large volumes of hot caustic liquors under pressure are great. The gelatinization and solution is not confined to very finely divided silica, as fused quartz tubes and quartz crystals also are attacked.

### SILICA GELS

**Setting Time.**—When a solution of sodium silicate is neutralized with an acid, sooner or later a gel is formed unless the

<sup>31</sup> *J. Am. Chem. Soc.*, **43** (1921), 391.

<sup>32</sup> LIEBIG: *Ann. chem. pharm.*, **102** (1857), 101; CAPITAINE: *Dinglers polytech. J.*, **222** (1876), 363.

solution is very dilute. The speed of gelation is dependent on the concentration, the excess of acid or of alkali present, agitation, the temperature, the impurities, the kind of acid used, and perhaps other factors. Flemming<sup>33</sup> studied this problem very thoroughly. He found that increasing both the temperature and concentration of silica decreased the time required for gelation. With neutral and slightly alkaline sols, raising the temperature from 18 to 25° about halved the setting time. The effect of temperature was greater with alkaline than with acid sols. A sol containing 0.270 mol of silica per liter set in 0.81 minutes, while one of half the concentration required 34.45 minutes.

Sols made with hydrochloric acid set more rapidly than those made with sulfuric acid at equivalent concentrations. Thus, with 0.45 mol of acid per liter the hydrochloric gel set in 2,910 minutes and the sulfuric gel in 3,420 minutes; with 0.15 mol of acid, the values were 9,975 and 11,100 minutes respectively. This may have been due to the different peptizing or coagulating effects of the sodium chloride and sulfate. The impurities present in the commercial sodium metasilicate used by Flemming affected the time of gelation. With alkaline sols the shape of the curves was the same, but the set was more rapid with that made from the commercial salt. Acid sols of this salt set more rapidly when the excess of acid was small (less than 1.25 mols per liter) and more slowly when the excess was large.

**Isoelectric Point.**—Flemming used his studies on the effect of an excess of acid or alkali to determine the isoelectric point of silica. With an excess of alkali, added as metasilicate, the setting time gradually increases from 1 minute at this point to 26 minutes at 0.225 mol of alkali as NaOH. As the sol passes from the isoelectric point through the neutral point and becomes slightly more acid, the time of gelation increases from minutes into hours and days, passing through a maximum at about 0.1 mol excess of hydrochloric acid per liter and then decreasing again. The isoelectric point was at an alkali concentration equivalent to 0.025 mol of sodium hydroxide per liter. This determination, however, is subject to at least two errors: (1) Sodium metasilicate was added to give the excess of alkali, thereby chang-

<sup>33</sup> *Z. physik. Chem.*, **41** (1902), 427.



ing the concentration of silica. (2) It is doubtful whether this salt is completely hydrolyzed at these concentrations,<sup>34</sup> so that the alkali equivalent probably is not correct. Another possible error is in the use of methyl orange as an indicator, since it changes color on the acid side.<sup>35</sup> Electrometric titrations by the writer indicate this error is very small.

Agitation hastened the set. Another factor, which has not been studied, is the effect of the ratio of sodium oxide to silica in the silicate solutions used.

It seems reasonable that the adsorption of various substances by silica gel is largely a physical phenomenon.<sup>36</sup> The structure of the gel and, therefore, its adsorptive capacity probably are affected by all the factors mentioned above. Even when the gel is secured, the conditions of drying have a tremendous influence on its properties. Can the contradictory results reported about silica gel be wondered at?

**Drying.**—Behr and Urban compared silica gel dried in four different ways with powdered quartz which had been boiled in hydrochloric acid.<sup>37</sup> The gel was prepared by Patrick's method<sup>38</sup> and washed free of chlorides. It was divided into four portions which were (1) dried at 25° in vacuum over P<sub>2</sub>O<sub>5</sub>, (2) heated to constant weight at 300°, (3) ignited at 1,000°, and (4) evaporated several times with hydrochloric acid and then ignited. The last two had crystallized, the fourth more than the third. The adsorption of water decreased as the crystallization increased, until there was no adsorption with either the last or the quartz. In all the cases where there was adsorption, the hydration and dehydration curves showed hysteresis.<sup>39</sup> The amount of water

<sup>34</sup> Cf. BOGUE, R. H.: *J. Am. Chem. Soc.*, **42** (1920), 2575.

<sup>35</sup> Methyl orange is a satisfactory indicator to use with sodium silicate solutions to determine the total Na<sub>2</sub>O content. The end point is sharp and clear and much more easily seen than with sodium carbonate solutions. Brom phenol blue may also be used. Phenolphthalein is not satisfactory, as it gives a fading end point with less than the total Na<sub>2</sub>O.

<sup>36</sup> PATRICK: Chicago Meeting, Am. Chem. Soc., 1920.

<sup>37</sup> *Z. angew Chem.*, **36** (1923), 57.

<sup>38</sup> MCGAVACK and PATRICK: *J. Am. Chem. Soc.*, **42** (1920), 946. A more complete account of this method was promised, but has never appeared so far as the writer knows.

<sup>39</sup> See below.

adsorbed by the amorphous silica gels was greater than that taken up by activated charcoal. The gel ignited at 1,000° adsorbed more than charcoal, up to 70 per cent relative humidity. These examples show how important the method of drying is. Similar results are shown with other vapors.

**Adsorption.** *Water.*—Van Bemmelen<sup>40</sup> was the first to study the power of adsorption of water by silica gel. He found no evidence of definite hydrates, although there were breaks in the vapor tension curves. These breaks, however, could be displaced by varying the age and the rapidity of hydration of the gel. Starting with a plastic gel containing 20 molecules of water to 1 of silica, and drying slowly, the gel remained transparent. At about 1.5 to 2 molecules of water there was a break in the curve and the gel became opaque. At about 0.6 to 0.9 molecules of water the gel became translucent and remained that way during the rest of the drying. When the gel was again exposed to water vapor, it followed the dehydration curve back to where the gel originally became translucent. Then the amount of water in the gel became less for a given vapor pressure than it had been on drying. The curve, however, again showed a break at which the adsorption of water became decidedly less rapid. If the gel was again dehydrated, it lost water at a constant weight, until it came to the original dehydration line. This occurred at the point at which the gel originally became opaque. The second dehydration then followed the same course as the original. Upon aging, the opacity and the break were secured with a higher water content, but the shape of the curve was similar.

Calcined silica gave the same form of hysteresis curve but the total amount of water adsorbed was less. Originally, this raised the question whether the colloidal silica was not simply extremely fine particles of anhydrous silica which took up water like a porous body. The decrease with calcination was explained as due to the agglomeration of the particles. As mentioned above, Behr and Urban found it was due to the crystallization of the silica.

There are many variables which affect the adsorption of water, but the following examples<sup>41</sup> show the action: A gel containing

<sup>40</sup> *Z. anorg. Chem.*, **13** (1896), 233.

<sup>41</sup> MILLER, E. B.: *Trans. Am. Inst. Chem. Eng.* **13** (1920), 379.

7 per cent residual water adsorbed 25.7 per cent of water from air saturated at 30°. The efficiency of the removal was 99 per cent until the gel had adsorbed 21.5 per cent of its weight of water. With air of 50 per cent humidity, the gel would only take up 22.5 per cent and the efficiency dropped rapidly when the gel had taken up 17.3 per cent water. With 26.7 per cent, the break comes when the gel reaches about 11 per cent moisture. The air passed at 50 cc. per minute per gram of gel in all these cases. When the rate was doubled and the temperature lowered to 20°, the efficiency began to fall off sooner but the total water adsorbed was greater. When the rate at which the air passed exceeded 30 cc. per minute per gram of gel (960 cu. ft. per minute per ton), the rate of drying very nearly reached a maximum. The drying was about 60 per cent more rapid at 125 than at 105°.

*Petroleum.*—It has been proposed to use silica gel in refining petroleum products and it has recently been announced that one of the oil companies is to use the process.<sup>42</sup> The gel may be used for two purposes, *viz.*, to remove sulfur compounds and to adsorb gasoline vapors. When the sulfur is removed with gel instead of sulfuric acid, the unsaturated compounds are not destroyed and the removal of sulfur compounds is greater. For this purpose the gel is powdered to about 200 mesh to speed up the adsorption so it becomes practical. The gel and the oil are agitated together, then filtered on a continuous rotary filter. In the experimental plant<sup>43</sup> at Baltimore this process is gone through three times, the gel and the oil moving in counter currents. The spent gel contains oil and impurities. It passes to a multiple-hearth, muffle-heated activator where the oil is driven off and condensed. The gel has to be given a further treatment to burn off the impurities. It is then sent back to purify more oil. It is claimed that the cost of treatment is less than that with sulfuric acid.

When kerosene purified by this method was tested, it was evident that it is the sulfur compounds, not the unsaturated ones, which are responsible for the soot and smoke. When gasoline

<sup>42</sup> Royal Dutch Shell Company, San Francisco, California. Refinery has been built at New Orleans, Louisiana.

<sup>43</sup> MILLER, E. B.: *Trans. Am. Inst. Chem. Eng.* (1923); Silica Gel Corp'n. *Bull.* 4, 1923.

purified by gel was used in an engine, there was much less carbon than when ordinary gasoline was used. Motor benzol gave similar results.<sup>44</sup> When the highest grade gasoline was used, gel-refined lubricating oils gave only about half as much carbon as the best ordinary oils, and about a fifth as much as the poor grades.

*Sulfur Dioxide.*—The adsorption of sulfur dioxide has been very thoroughly studied by McGavack and Patrick.<sup>45</sup> The amount of gas taken up increased as the temperature decreased. This increase became very great below 30°. The adsorption, except at very low temperatures, follows Freundlich's adsorption law. When all the air was removed from the gel, the adsorption of sulfur dioxide was reversible, instead of showing hysteresis as water does. The time required to reach equilibrium in the presence of air is a matter of hours instead of minutes, as in a vacuum. Under these conditions, the action is not strictly reversible. The maximum adsorption was secured with a gel containing about 7 per cent water.

*Ammonia.*—Similar experiments have been made with ammonia.<sup>46</sup> Reducing the water content of the gel from 4.93 to 0.33 per cent cut the amount of ammonia adsorbed 53 cc. per gram on the average. It was found that the gel adsorbed the nitric acid used in its purification so strongly that it could only be removed by heating at a high enough temperature to remove most of the water. The adsorption of ammonia was much stronger than that of sulfur dioxide. A large part of this was due to the water and acid present in the gel. In fact, it was concluded that with an anhydrous gel the adsorption of ammonia would be "in accordance with its ease of condensation as expressed by its critical temperature."

*Nitric Oxide.*—Daniels and McCollum<sup>47</sup> propose to adsorb nitric anhydride with silica gel in the arc process for the fixation of nitrogen. The removal is complete, permitting recirculation of the gases and economical recovery of concentrated nitric acid.

<sup>44</sup> FIELDNER and JONES: Bur. Mines Serial No. 2517 (1923).

<sup>45</sup> *J. Am. Chem. Soc.*, **42** (1920), 946.

<sup>46</sup> DAVIDHEISER and PATRICK: *J. Am. Chem. Soc.*, **44** (1922), 1.

<sup>47</sup> *Ind. Eng. Chem.*, **15** (1923), 1173.



*General Equation.*—The adsorption of gases by silica gel is a purely physical phenomenon. Qualitatively, the volume of gas adsorbed is proportional to the ratio of the partial pressure of the gas to the vapor pressure of the gas condensed to a liquid at the temperature of adsorption. Quantitatively, this relationship is

$$V = K \left( \frac{P\sigma}{P_0} \right)^{1/n}$$

where  $V$  = cubic centimeter of liquefied gas adsorbed

$\sigma$  = the surface tension of this liquid

$P_0$  = the vapor pressure of the liquid

$P$  = equilibrium pressure in centimeters of mercury  
and  $K$  and  $1/n$  are constants.

**Structure.**—These findings are in accord with Zsigmondy's views<sup>48</sup> on the structure of the gel. He considers that the gel contains multitudes of amicroscopic pores. This is based on the fact that at times the gel is practically optically clear, even in the ultramicroscope. The few submicrons present were probably due to irregularities in the gel. This idea is not at all in accordance with that of Bütschli. The latter, by treating the gel with a mixture of chloroform and cedarwood oil and allowing the first to evaporate, secured a structure which was visible under the microscope. Zsigmondy decided this appearance was due to alternate portions of the gel either saturated with liquid or from which the liquid had evaporated. If the lowering of the vapor pressure of water by adsorption in the gel is caused by capillary action of the pores, the average diameter necessary for the observed effect is calculated to be  $5\mu$ . This agrees with the amicroscopic conception.

The fact that the gel acts as an ultrafilter toward colloids while permitting the free passage of electrolytes is further evidence in favor of this theory. For example, a silver mirror can be formed on the surface of the gel by placing it in a silver sol. This, of course, may be due to adsorption of the silver but in that case the formation of a continuous film, necessary for a mirror, would not be expected.

<sup>48</sup> *Z. anorg. Chem.*, **71** (1911), 356.

Bachman<sup>49</sup> extended the evidence in favor of Zsigmondy's theory by showing that the weights of various liquids which are adsorbed are in proportion to their specific gravities. The volume of liquid adsorbed from a saturated vapor is the same as that taken up from the liquid.

**Improvements.**—In view of the fact that there are so many variations in the preparation of the gel which affect its properties, the question arises whether the present form of gel is the best. Briggs<sup>50</sup> dried unwashed gel containing sodium chloride at 300° and plunged it while still hot into hot distilled water. The gel was then washed free of hydrochloric acid by decantation. Then it was dried again at 300° and the process repeated until all the chloride had been removed. The adsorptive capacity of this gel for nitrogen at -190° was more than 60 per cent greater than that of a very good grade of adsorbent charcoal.

Holmes<sup>51</sup> has reported that he was able to secure a gel by treating sodium silicate with nickel chloride, which would adsorb 100 per cent of its weight of benzene. Ray<sup>52</sup> states that ordinary silica gel only takes up about 23 per cent of its weight of benzene. This certainly is an indication that there are further possibilities with specially prepared silica gels.

<sup>49</sup> *Z. anorg. Chem.*, **79**, (1913), 202.

<sup>50</sup> *Proc. Royal Soc.*, **100A** (1921), 88.

<sup>51</sup> New Haven Meeting, Am. Chem. Soc., 1923.

<sup>52</sup> *Chem. Met. Eng.*, **29** (1923), 354.

# CHAPTER XXV

## THE COLLOID CHEMISTRY OF THE CEREALS

By

CARL L. ALSBERG

WHEAT<sup>1</sup>

The proteins of the wheat kernel are five in number, namely, gliadin, glutenin, the albumin, leucosin, a globulin similar in composition and properties to the globulins found in many seeds, and a proteose. Recently Jones and Gersdorff<sup>2</sup> have investigated wheat bran freed by agitation in water from adherent flour, and found a globulin, an albumin, and a prolamin in it. Whether or not these proteins are identical with the corresponding proteins of the germ and endosperm has not yet been determined. There is some evidence that they are not. It is noteworthy that Jones and Gersdorff obtained no glutenin from bran. Neither leucosin nor the globulin present anything distinguishing them from plant albumins and globulins generally. They will not be considered further.<sup>3</sup>

**Gliadin.**—Gliadin<sup>4</sup> is a prolamin, soluble in dilute and fairly

<sup>1</sup> Most of our strictly chemical knowledge of wheat proteins is due to the classic work of T. B. Osborne. (The proteins of the wheat kernel, Carnegie Inst. of Wash., 1907.) Much of what is here presented is quoted from this monograph.

<sup>2</sup> Proteins of wheat bran. I. Isolation and elementary analyses of a globulin, albumin, and prolamin, *J. Biol. Chem.* **58** (1923), 117.

<sup>3</sup> For the general properties and composition of plant proteins, the reader is referred to OSBORNE, T. B.: "The Vegetable Proteins," Longmans, Green & Co., London and New York, 1909.

<sup>4</sup> The following paper presents a full critical analysis of the work on the solubilities of the wheat proteins: BAILEY, C. H. and BLISH, M. J.: Concerning the identity of the proteins extracted from wheat flour by the usual solvents, *J. Biol. Chem.*, **23** (1915), 345.

strong alcohol. These solutions become cloudy on standing.<sup>5</sup> The solubility increases with the strength of the alcohol, up to a certain maximum and then decreases. The presence of other substances, for example, sugar,<sup>6</sup> influences its solubility. Gliadin is soluble in other dilute alcohols, such as methyl, propyl, and benzyl alcohols, in phenol and paracresol, and also in pure glacial acetic acid. It can be prepared directly from flour, dough, or gluten (see below) by extraction with aqueous alcohol. The alcoholic solutions are more viscous than suspensions prepared by diluting alcoholic solutions with water.

Gliadin is soluble in very dilute acids, for it forms salts soluble in water, and its solubility in ordinary distilled water is stated to be due to carbon dioxide.<sup>5,7</sup> It can be dissolved out of flour by very dilute acid. Nasmith<sup>8</sup> was the first to show that the addition of a further very minute amount of acid produces a cloudy precipitate of gliadin without precipitating glutenin, if present. The precipitate separated more completely on heating but redissolved to some extent on cooling. He regarded the precipitate as insoluble gliadin chloride. Rona and Michaelis<sup>9</sup> reported that an insoluble hydrochloride is formed due to the crowding back of the dissociation by the excess of acid. Lüers,<sup>5</sup> employing suspensions made by diluting alcoholic solutions of gliadin with water, found that traces of acid sufficient to give the suspension a normality of  $\frac{N}{100,000}$  flocculate the gliadin. The floccules agglutinate and form a tough viscous mass. Further addition of acid gradually clears up the suspension, dispersing the coagula until there

<sup>5</sup> LÜERS, H.: Beiträge zur Kolloidchemie des Brotes, III. Kolloidchemische Studien am Roggen- und Weizengliadin mit besonderer Berücksichtigung des Kleber- und Backfähigkeitsproblems, *Kolloid-Z.*, **25** (1919), 177.

<sup>6</sup> JAGO, WM. and JAGO, WM. C.: "The Technology of Bread-making," London, 1911, p. 316.

<sup>7</sup> LÜERS, H.: *Op. cit.*, p. 181; OSBORNE, T. B.: Die Pflanzenproteine, *Ergebnisse Physiol.*, **10** (1910), 66.

<sup>8</sup> The chemistry of wheat gluten, University of Toronto Studies, Physiological Series, 1903, reprinted from *Trans. Can. Inst.*, vol. VII.

<sup>9</sup> RONA, P. and MICHAELIS, L.: Beiträge zur allgemeinen Eiweisschemie II. Mitteilung. Über die Fällung der Globuline im isoelektrischen Punkt, *Biochem. Z.*, **28** (1910), 198.



is clear solution at a normality of about  $\frac{4}{10,000}$  with a pH of about 4. Further addition of acid causes first opalescence and at  $\frac{N}{100}$  to  $\frac{N}{10}$  (about pH 2) a second coagulation without agglutination. Sulfuric acid produces the second precipitation at  $\frac{5}{10,000}$  normal, while lactic does not produce it at all in the concentrations of gliadin examined. The viscosity changes accompanying these phenomena are what would be expected. In the region of the first coagulation the viscosity is difficult to measure; but there seems to be a viscosity minimum at about pH 5.7 when hydrochloric acid is used. Then there is a sharp rise in viscosity to a maximum at about pH 3, followed by an almost equally rapid drop. Dilution of the hydrochloric acid gliadin suspensions lowers viscosity. The viscosity of suspensions free from added acid is increased by warming. At 8° to 9° it is not measurable because of coagulation.

In dilute alkali, gliadin is soluble. It is precipitated unchanged by neutralization as well as by the addition of a suitable amount of sodium bicarbonate.<sup>7</sup> The addition of traces of alkali to gliadin suspensions causes no precipitation. Sodium hydrate does not flocculate at any concentration, while barium hydrate does so at  $\frac{N}{100}$ . In both cases the viscosity increases with the addition of alkali. Viscosity reaches a maximum at about  $\frac{N}{1,000}$  sodium hydroxide. At greater concentrations there is a slight decrease and the solution becomes slightly opalescent.<sup>5</sup>

The addition of neutral salts to solutions of acid gliadin rapidly lowers the viscosity and diminishes the degree of dispersion until coagulation sets in. The salt concentration at which coagulation occurs depends upon the character of the anion. Chlorides are least effective, phosphates more so, while sulfates act far more powerfully than either. Tartrates are still more effective than sulfates. This electrolyte effect explains why gliadin is less soluble in salt solutions than in ordinary distilled water, which contains dissolved carbon dioxide. The

effect which neutral salts have upon alkali gliadin is similar; only in this case, since the gliadin is negatively charged, it is the cation which has the predominating action, univalent cations being less effective than polyvalent ones.

Rona and Michaelis<sup>9</sup> determined the isoelectric point of gliadin by the precipitation method to be about  $5.9 \times 10^{-10}$ . The accuracy of this determination is, by inference, questioned by Michaelis in a later paper,<sup>10</sup> in which he omits gliadin from the list of the proteins, the isoelectric points of which had been determined accurately. Lüers<sup>5</sup> found in cataphoresis experiments that gliadin in suspension wandered to the anode at pH 9.05, to the cathode at pH 5.98, and did not migrate in either direction at pH 6.70. He concluded that the isoelectric point for his preparation was very close to the neutral point.

There seems to be but one kind of gliadin in all wheats, for the composition and chemical behavior are always the same,<sup>11</sup> as are the racemization curves,<sup>12</sup> viscosity, surface tension, Zsigmondy "gold number," and the power to act as a protective colloid as determined by the method of Groh.<sup>13</sup> The alcohol soluble bran protein of Jones and Gersdorff is probably not gliadin, however.

Gliadin is much less easily converted into insoluble products than are most other proteins. Its solutions in 70 per cent alcohol can be boiled for an indefinite time, and even concentrated until much of the alcohol has been removed, without forming insoluble products, but heating to 130° in the autoclave renders it insoluble in alcohol. On heating with very weak alcohol or with water, this protein is gradually altered and becomes insoluble in stronger alcohol, but the coagulated gliadin thus formed is in appearance unlike the heat coagulum formed by most other proteins.

<sup>10</sup> MICHAELIS, L.: Zur Theorie des isoelektrischen Punktes. III. Mitteilung. Das Wesen der eiweissartigen kolloidalen Lösungen, *Biochem. Z.*, **47** (1912), 258.

<sup>11</sup> WOOD, T. B.: The chemistry of strength of wheat flour, *J. Agr. Sci.*, **2** (1907), 267.

<sup>12</sup> WOODMAN, H. E.: The chemistry of the strength of wheat flour, *J. Agr. Sci.*, **12** (1922), 231.

<sup>13</sup> GROH, J. and FRIEDL, G.: Beiträge zu den physikalisch-chemischen Eigenschaften der alkohollöslichen Proteine des Weizens und Roggens, *Biochem. Z.*, **66** (1914), 154.

Woodman<sup>12</sup> found that, as determined by the method of Foreman,<sup>14</sup> gliadin has a combining weight of approximately 5,000, and its molecule probably contains three, or a multiple of three, carboxyl groups. On the assumption that its molecule contains 5 atoms of sulfur, Osborne<sup>3</sup> assigned to it a minimum molecular weight of 15,568.

**Glutenin.**—Glutenin is a glutelin practically insoluble in water and alcohol. It is quite soluble in dilute acids and alkalis and is precipitated on neutralization. It coagulates at about 70°; is modified by drying and by treatment with alcohol.<sup>15</sup> Woodman found that the specific rotation of a sample of dry powdered glutenin from Manitoba hard wheat, when dissolved by warming to 37° in quarter normal aqueous NaOH, was  $(\alpha)D = -99.5^\circ$ , while glutenin from English soft wheat under the same conditions gave  $(\alpha)D = -78^\circ$ . As the incubation at 37° continued, the two glutenins gave different racemization curves. Hence, Woodman concluded that there are different glutenins in different wheats.<sup>12</sup> It should be noted, however, that these observations indicate nothing concerning the physical properties of different glutenins. It is not inconceivable that glutenins which differ chemically in the manner discovered by Woodman may yet resemble one another physically. Wheat is the only cereal which yields a protein with the physical properties of glutenin.

**Gluten.**—Gliadin and glutenin, when moistened as they occur together in flour, absorb water and hold together to a much greater extent than do the proteins of any other cereal. This property makes it possible to wash away most of the other constituents of wheat flour. The mixture of the two proteins that is left is known as gluten. Gluten thus prepared is commonly referred to as "crude" gluten, because it contains enmeshed, besides glutenin and gliadin, certain non-protein constituents of the flour, such as some starch, fat, and lipoid, as well as about twice as

<sup>14</sup> FOREMAN, F. W.: Rapid volumetric methods for the estimation of amino acids, organic acids, and organic bases, *Biochem. J.*, **14** (1920), 451.

<sup>15</sup> SHARP, P. F. and GORTNER, R. A.: The physico-chemical properties of strong and weak flours. V. The identity of the gluten protein responsible for the changes in the hydration capacity produced by acids, *J. Phys. Chem.*, **27** (1923), 674.

much water by weight as protein. The amount of non-protein material in it differs from sample to sample. The amount of water retained mechanically varies, as does the water more firmly held by the proteins, commonly described as water of hydration.<sup>16</sup>

The physical properties of glutes obtained from different flours vary greatly. A *good* gluten is elastic, firm, and cohesive, and, when pulled, forms long, rope-like threads. It is not sticky. When flattened out, it has the power to recoil and tends to maintain a globular shape. It can be kneaded out into a thin, translucent mass. A *poor* gluten, on the other hand, is dark in color, flabby, non-resilient, very soft and sticky, and, instead of forming long threads upon being pulled out, breaks off squarely. The pieces are not rope-like but are flat and tape-like in appearance. A mass of poor gluten tends to run or spread out and has very little power to recoil.<sup>17</sup> Poor, soft gluten gives off its excess water much more easily to an absorbent surface, such as slate, than a good gluten.<sup>18</sup>

By virtue of its elastic, ductile, and tenacious properties, gluten is capable of being expanded enormously by any gas. A good gluten may be able to expand five times as much as a poor one.

It was at one time held that in gluten the two component proteins, gliadin and glutenin, are chemically combined. However, that there is a true chemical union in the ordinary sense of the term is improbable, for mere extraction with alcohol separates them.

While Balland states that gluten,<sup>19</sup> air-dried, recovers its weight and elasticity when placed in water, it is doubtful whether

<sup>16</sup> As J. Loeb ("Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Company, New York, 1922, p. 19) has pointed out, the term "hydration" is often used in a vague way to designate such phenomena as the swelling of proteins, which is an osmotic effect. The term should not be so used. In moist gluten undoubtedly some of the water is held by osmotic forces.

<sup>17</sup> SNYDER, H.: Human food investigations. The gluten of wheat, Minn. Agr. Expt. Sta. *Bull.* **54** (1897), 37-42.

<sup>18</sup> BREMER, W.: Ueber ein neues Verfahren zur schnellen Bestimmung der Trockensubstanz im Weizenkleber, *Z. Nahr.-Genussm.*, **14** (1907), 682.

<sup>19</sup> BALLAND: Mémoire sur les farines. III. Des causes de l'altération des farines, *J. Pharm. Chim.*, Series 5, **8** (1883), 501.



the original physical condition is regained, for Sharp and Gortner<sup>20</sup> found moist gluten which has once been dried does not absorb and swell again to its original extent. Dehydration in vacuo at 45° to 50°C. changes it so that the physico-chemical properties of good and poor gluten become more nearly alike. The character of this change is unknown, but it is significant that Cohn<sup>21</sup> found it almost impossible to wet the surface of proteins uniformly after they had been dried by alcohol and ether. Moist gluten dried at 100°, and then placed in water again, absorbs a part of the water lost but does not regain its elasticity.<sup>19</sup> Wet gluten heated to the coagulation temperature of glutenin, 70°C., is altered.

**Effect of Electrolytes on Gluten.**—Gluten is an emulsion colloid.<sup>11</sup> Like its constituent proteins, gluten is dispersed in weak acids and alkali, the rate increasing with the acidity. In acids, there is a maximum beyond which the dispersion diminishes until it reaches zero—"the critical point" of Wood and Hardy.<sup>22</sup> This is consistent with the behavior of gliadin as observed by Nasmith, Rona and Michaelis and by Lüers. At this "critical point" Wood and Hardy believe the excess of acid suppresses the feeble ionization of the protein-acid salt, thus causing the potential difference of the electric double layer surrounding the protein particles to disappear, thereby obliterating the forces making for dispersion.

In distilled water, gluten is somewhat soluble, due, apparently, mainly to the solubility of the gliadin.<sup>15</sup> Wood and Hardy,<sup>22</sup> however, believe gluten to be really insoluble in water, and its apparent solubility in ordinary distilled water to be due to dispersion by dissolved carbon dioxide. In such a solution the protein is electropositive—that is to say, it displays the characteristic relation of protein to acid. Moreover, it can be precipitated by a trace of alkali. The lesser solubility in salt solution as compared with ordinary distilled water is probably due to the

<sup>20</sup> Physico-chemical studies of strong and weak flours II. The imbibitional properties of the glutes from strong and weak flours, *J. Phys. Chem.*, **26** (1922), 101.

<sup>21</sup> Studies on the physical chemistry of the proteins. I. The solubility of certain proteins at their isoelectric points, *J. Gen. Physiol.*, **4** (1922), 699.

<sup>22</sup> WOOD, T. B. and HARDY, W. B.: Electrolytes and colloids—The physical state of gluten, *Proc. Roy. Soc. (London)*, Series B, **81** (1909), 38.

fact, shown by Wood and Hardy, that neutral salts within certain limits prevent or lessen the dispersion of gluten by acids and alkalies. Long ago Balland<sup>19</sup> showed that wet gluten treated with strong salt solution becomes tough and leathery, and, on washing out the salt, remains more elastic and coherent than it was before the salt treatment. This phenomenon is well known to bakers, who make soft doughs stiffer by the addition of salt. Naturally hard waters harden gluten considerably, while soft alkaline waters destroy the springiness of gluten by preventing the coherence of its particles.<sup>23, 24</sup> Calcium salts have an especial toughening effect.<sup>25</sup>

Wood and Hardy<sup>22</sup> have studied the cataphoresis of gluten and found that its isoelectric point probably lies between  $10^{-7}$  and  $10^{-8}$ N. Bailey and Peterson<sup>26</sup> report the isoelectric point of gluten to be pH 5.1. The manner in which this result was arrived at has not as yet been published. Sharp and Gortner speak of bringing dispersed gluten to the isoelectric point without stating what that point is. They believe that the hydrogen ion concentration for the optimum swelling of gluten is practically the same for different glutes and that this argues for little or no difference in the isoelectric points of glutes from different types of wheat.<sup>20</sup> As there are two proteins present in a somewhat variable ratio, and since gluten has never been prepared free from ash, starch, and possibly other constituents, it is evident that one cannot speak of any definite hydrogen ion concentration as the isoelectric point.

Gluten, being a mixture of ampholytes, may combine chemically with acids and bases like gelatin and other proteins,<sup>27</sup> in

<sup>23</sup> WHYMPER, R.: Colloid problems in bread making. Brit. Assoc. Advancement Sci., Rept. III. of the Committee on Colloid Chemistry and its General and Industrial Applications, (1920) p. 70.

<sup>24</sup> LÜERS, H. und OSTWALD, Wo: Beiträge zur Kolloidchemie des Brotes. II. Zur Viskosimetrie der Mehle, *Kolloid-Z.*, **25** (1919) 130.

<sup>25</sup> HENDERSON, L. J., FENN, W. O. and COHN, E. J.: Influence of electrolytes upon the viscosity of dough, *J. Gen. Physiol.*, **1** (1919), 387.

<sup>26</sup> Studies of wheat flour grades. II. Buffer action of water extracts, *J. Ind. Eng. Chem.*, **13** (1921), 916.

<sup>27</sup> HENDERSON, L. J., COHN, E. J., CATHCART, P. H., WACHMAN, J. D. and FENN, W. O.: A study of the action of acid and alkali on gluten, *J. Gen. Physiol.*, **1** (1919), 459.

harmony with the conceptions of Sørensen and his associates and of Loeb.<sup>16</sup> The acidity<sup>11, 20, 22, 28, 29</sup> and the presence of certain salts<sup>11, 25</sup> greatly affect the water absorption, that is, the imbibition and swelling of gluten, just as they do the swelling of gelatin disks. Upson and Calvin<sup>28</sup> found that disks cut from gluten washed out of flour with distilled water swell in acid, the maximum absorption being obtained with 0.005 N hydrochloric acid, 0.01 to 0.02 N lactic acid and 0.02 N acetic acid. The absorption is greatest in acetic acid, less in lactic, and nearly as great in hydrochloric as in lactic acid. In greater concentrations the absorption becomes less, but the curves charted from the data do not fall off at anything like the same rate for the three acids, that for hydrochloric acid falling off most rapidly. Gluten seems to be a unique mixture in that there is an optimal swelling in "weak" acids. No pure protein is known to behave in this way. In 0.2 N and 0.5 N hydrochloric acid the disks actually lose water and become tougher and more elastic, just as in salt solutions. Such disks swell when placed in more dilute acid. In dilute acids there is a certain amount of dispersion. The taking up and giving up of water is largely reversible.

When any salt is added, the swelling in acid is much reduced, and, indeed, in the higher concentrations of certain salts the disks drop to a weight below that of the original moist disk. Glycocoll behaves like a salt, though the effect is less marked. Non-electrolytes like sucrose are comparatively ineffective except in high concentrations. These observations are in harmony with those of Wood and Hardy,<sup>22</sup> Gortner and Doherty,<sup>29</sup> Sharp and Gortner,<sup>20</sup> and Lüers and Ostwald.<sup>30</sup> Sharp and Gortner determined the hydrogen ion concentration at which the maximum imbibition occurs as being pH 3.25 to 2.25, and this agrees with the gliadin viscosity experiments of Lüers. They found the action of alkali upon gluten to be somewhat different from that

<sup>28</sup> UPSON, F. W. and CALVIN, J. W.: On the colloidal swelling of wheat gluten, *J. Am. Chem. Soc.*, **37** (1915), 1295, Fig. 3, pl. II; also, The colloidal swelling of wheat gluten in relation to milling and baking, *Nebr. Agr. Expt. Sta. Research Bull.* **8** (1916), Fig. 5.

<sup>29</sup> GORTNER, R. A. and DOHERTY, E. H.: Hydration capacity of gluten from "strong" and "weak" flours, *J. Agr. Research*, **13** (1918), 389, Fig. 17.

<sup>30</sup> LÜERS, H. und OSTWALD, W.: Beiträge zur Kolloidchemie des Brotes. V. Die kolloide Quellung des Weizenklebers, *Kolloid-Z.*, **27** (1920), 34.

of acids. In acids of suitable concentration gluten swells with relatively little dispersion, while, in alkali, imbibition and dispersion follow one another so closely that in some concentrations they compensate one another. Measurement of imbibition is possible only if the gluten is left in very weakly alkaline solutions for a very short time. Under such conditions  $\frac{1}{200}$  M sodium sulfate lessens the imbibition.

The preparations of gluten used for these imbibition studies by Upson and Calvin, Gortner and Doherty, and Sharp and Gortner were not free from ash. This is plain from the analyses of their gluten preparations published by Sharp and Gortner. Now, according to Procter<sup>31</sup> and Procter and Wilson,<sup>32</sup> the degree of swelling of a gel is conditioned by the excess of diffusible ions in the gel over those in the water layer. This hypothesis has been accepted by J. Loeb,<sup>16</sup> and it follows, as pointed out both by J. Loeb and by C. R. Smith,<sup>33</sup> that, to determine the properties of a gel—at least quantitatively—gels free from ash should be employed. Indeed, Henderson and his associates<sup>27</sup> have presented evidence indicating that there is a tendency for gluten to swell more in acid, the greater, relatively, the amount of electrolyte present in the swollen mass. For the present, then, the data on record concerning the swelling of gluten must be regarded as qualitative only.

Henderson, Cohn, Cathcart, Wachman, and Fenn,<sup>27</sup> with the help of a special instrument, have studied the viscosity of swollen gluten which had previously been dried. What was measured was rather the resistance of the gluten to stirring than what is ordinarily termed "viscosity." A well-marked minimum of "viscosity" near a hydrogen ion concentration corresponding to pH 5.7 was found. This minimum, while due chiefly to the hydrogen ion concentration, is in a secondary manner influenced by the amount of electrolyte present. The electrolyte concen-

<sup>31</sup> PROCTER, H. R.: The equilibrium of dilute hydrochloric acid and gelatin, *J. Chem. Soc.*, **105** (1914), 313.

<sup>32</sup> PROCTER, H. R. and WILSON, J. A.: The acid-gelatin equilibrium, *J. Chem. Soc.*, **109** (1916), 307.

<sup>33</sup> SMITH, C. R.: Osmosis and swelling of gelatin, *J. Am. Chem. Soc.*, **43** (1921), 1350.



tration determines the great variation in viscosity measurements in systems where the protein is suspended in distilled water. It also appears to be largely variable with time, so that a process of "setting" may be suspected. It does not coincide with the isoelectric point; nor does it correspond with the true swelling or hydration. Perhaps it is identical with the above-described gliadin viscosity minimum of Lüers, due to flocculation.

**"Development" of Gluten.**—When flour is mixed with water, it does not at once form dough. Some time must elapse before the maximum plasticity is developed. The baker speaks of this as the time necessary to "develop" the gluten. Bénard and Girardin<sup>34</sup> and Balland<sup>19</sup> showed that the amount of gluten that can be washed from dough allowed to stand increases to a maximum in most flours and then decreases. The ultimate decrease is due to solution of protein. Kneading the dough during development affects the results, and warming to 40° speeds up the "development" of the gluten. Low temperatures (8 to 9°) inhibit "development." "Development" increases the yield of moist gluten as well as the yield on the water-free basis. During "development" the dough acidity increases and also the "hydration" of the gluten. It becomes softer and holds more water. Old flours lose more gluten during washing than new flours. Indeed, in such flours the gluten yield may decrease from the beginning of "development" without passing through a maximum. From some flours, particularly very old flours of low-protein content, little or no gluten can be washed. Jessen-Hansen<sup>35</sup> has shown that the gluten has not disappeared from such flours, but that, if the acidity be suitably reduced, perfectly normal gluten is obtained. It is, in the light of present-day knowledge, altogether likely that the aging or maturing of flour, which up to a certain point vastly improves its baking quality, depends, in the main, upon the development of an optimum acidity to give the gluten the physical properties best for baking.

<sup>34</sup> Sur le dosage du gluten dans les farines, *J. Pharm. Chim.*, **4** (1881), 127.

<sup>35</sup> Etudes sur la farine de froment. I. Influence de la concentration en ions hydrogène sur la valeur boulangère de la farine, *Compt.-rend. trav. lab. Carlsberg*, **10** (1911), 170.

It was at one time thought that, because time is necessary to "develop" gluten, gluten does not exist as such in flour but is formed by enzyme action from a precursor. This hypothesis has today no basis.<sup>1</sup> It is probable that the time necessary to "develop" the gluten is merely the time necessary to permit of the process of imbibition to take place. Perhaps a process akin to "setting" is also involved (see above). A review of the factors above enumerated, which hasten "development," shows that they are all factors favoring imbibition. They explain why different flours have different optimum "development" times. It would be interesting to dough different flours with buffer solutions of definite hydrogen ion concentrations and electrolyte content to determine whether or not under such conditions they would show similar optimum "development" times, having in mind their varying protein content.

**Theories Concerning Gluten Quality.**—Opinions differ concerning the causes which determine the differences in the physical properties of glutes. It was at one time held that the cause was variation in the ratio of the gliadin to the glutenin in the gluten. The determination of the glutenin-gliadin ratio was usually made upon gluten prepared by washing, on the assumption that in it this ratio would be the same as in flour. It is obvious that this need not be so because of the variable dispersion of the two proteins dependent upon the reaction of the flour and the character and quantity of wash water. Bailey and Blish,<sup>4,36</sup> using a new method, concluded that the glutenin-gliadin ratio does not differ significantly in different wheats. Sharp and Gortner<sup>37</sup> found no relationship between the various protein fractions of the flour and the volume of the loaf produced from it; their "data indicate that gliadin and glutenin are present in wheat flour in approximately equal amounts."

It would seem that Wood, Upson and Calvin, and Gortner and collaborators agree that the character of the gluten is predeter-

<sup>36</sup> BLISH, M. J.: On the chemical constitution of the proteins of wheat flour and its relation to baking strength, *J. Ind. Eng. Chem.*, **8** (1916), 138.

<sup>37</sup> SHARP, P. F. and GORTNER, R. A.: The physico-chemical properties of strong and weak flours. VI. The relation between the maximum viscosity obtainable by the addition of lactic acid and the concentration of flour-in-water suspensions, *J. Phys. Chem.* **27** (1923), 771.

mined in the seed. Gortner and his collaborators believe that this predetermination consists in the formation, for one thing, of a glutenin of varying colloidal qualities. They believe that the glutenin very largely determines the behavior of gluten,<sup>15</sup> wherein they are in accord with Guthrie,<sup>38</sup> but not with Osborne,<sup>1</sup> Lüers,<sup>5</sup> Wood and Hardy,<sup>22</sup> or Guess.<sup>39</sup> The other investigators above mentioned believe that the predetermination of gluten character depends upon the kinds and concentration of the electrolytes, in the presence of which it is formed. The latter factor may be modified during the course of flour manufacture. Gortner's recent investigations on a series of flours, three pairs of which were of high and low extraction from the same wheats, indicate that his glutenin "quality" factor is not affected by flour manufacture.

At any rate, no final judgment can as yet be formed concerning all the factors which may determine the physical properties, that is, the "quality" of gluten.

**Starch.**—Wheat starch was formerly assumed to be identical with all other starch. Only in recent times has it been recognized that each starch has its individual characteristics. At this time the colloid properties of starch in general cannot be described in detail. Mention can only be made of such specific properties of the cereal starches as have been put on record. They are few. The gelatinization temperature of wheat starch is given by Lippmann as 62.5° to 64.0°; by Reichert as 62.9° to 64.0°.<sup>40</sup> According to Rodewald, the density is 1.5072 to 1.4860 and the water absorption at 0°, when quite dry, 31.63 per cent, with a heat of wetting of 28.78 cal. per gram. Its specific heat on the dry basis is 0.2697; with a water content of 33.63 per cent, it is 0.3054. Commercial wheat starch contains 0.23 per cent of mineral matter.<sup>41</sup> Its solutions prepared by heating with water under

<sup>38</sup> GUTHRIE, F. B.: The absorption of water by the gluten of different wheats, *Agr. Gaz. N. S. Wales*, **7** (1897), 583.

<sup>39</sup> GUESS, H. A.: The gluten constituents of wheat and flour and their relation to bread making qualities, *J. Am. Chem. Soc.*, **22** (1906), 263.

<sup>40</sup> REICHERT, E. T.: The differentiation and specificity of starches in relation to genera, species, etc., Carnegie Institution Publication **173**, Washington (1913).

<sup>41</sup> TADOKORO, T. and SATO, S.: On the differences between some colloidal properties of common and glutinous rice starch, *J. Coll. Agr. Hokkaido Imp. Univ.* (Sapporo, Japan), **13** (1923), 1.

pressure have been studied by Samec and Haerdtl.<sup>42</sup> Rask and Alsberg<sup>43</sup> found the viscosities of the gelatinized starches from different varieties of wheat to be very different. Thus, for a 5.5 per cent suspension, they found the maximum and minimum viscosities for winter wheats at 90° to be, respectively, 213 and 132 centipoises, and for spring wheats, 124 and 51 centipoises. Durum wheat starch is intermediate between the two. They found that gelatinized starch in 3 per cent pseudo-solution had a pH of 5.2 to 5.6. At equal fluidities, wheat starch gives a paste of mush-like consistency as compared with potato or corn starch.<sup>44</sup>

Other colloid carbohydrates, such as cellulose, pentosan, and lignin, are present in the wheat berry but they have been but little studied.

**Nucleic Acid.**—Tritico-nucleic acid is found in the germ.<sup>45</sup> It has a molecule of large size and its solution exhibits colloidal properties. It is not soluble as a free acid in cold water. In boiling water it forms a pasty mass, of which very little is soluble. By boiling it is altered. Its salts with the alkali metals are soluble and, when precipitated from their solutions, the precipitates formed are often voluminous and gelatinous. It is polybasic and, once it has combined with a base, it is practically impossible to free it again.

**Flour Strength.**—Bakers speak of "strong" and "weak" flour. It is very difficult to give a wholly satisfactory definition of what is meant by "strength" and "weakness." For present purposes it is sufficient to point out that, in general, the baker regards that flour as the "strongest" from which the most bread of the best quality can be made. It is obvious, therefore, that strength is the resultant of many factors, of which only those of a colloid chemical nature can be considered here. Fermentation problems, for example, lie beyond our sphere.

<sup>42</sup> Studien über Pflanzenkolloide. IX. Zur Kenntnis verschiedener Stärkearten, *Kolloidchem. Beihefte*, **12** (1920), 281.

<sup>43</sup> A Viscometric Study of Wheat Starches, *Cereal Chemistry*, **1** (1924), 7.

<sup>44</sup> BUEL, H.: A study of some of the physical properties of starches. VIII. International Congress of Applied Chemistry, **13**, 63.

<sup>45</sup> OSBORNE, T. B. and HARRIS, I. F.: Die Nucleinsäure des Weizenembryos, *Z. Physiol. Chem.*, **36** (1902), 85.



**Dough.**—The yield of bread depends, in the main, upon the amount of gluten present and upon its imbibition power, since, in holding water, gluten plays the major and starch the minor part. Of two flours with identical gluten, that one will yield the more dough which has the greater gluten content.<sup>46</sup> Since hydrogen ion concentration and electrolyte content influence the swelling of gluten, one would expect the optimum hydrogen ion concentration of dough for baking to increase water absorption, but Jessen-Hansen<sup>35</sup> states that this is not the case. Fuller understanding of the water capacities of flour can hardly come until accurate methods are used to determine dough texture. Dough is not viscous, as this term is applied to liquids.<sup>6, 25</sup> It is more properly termed "plastic,"<sup>47, 48</sup> The laws of plastic flow are not the same as those of viscous flow.<sup>49</sup> A certain internal friction, known as the "yield value," must be overcome to start plastic flow. It might be of great interest to determine both the yield values and the mobilities of doughs under a variety of conditions. All one can say at present concerning the factors controlling water absorption is that the question requires reinvestigation upon isoplastic doughs.

While plastometric studies have not been made upon doughs, Henderson, Fenn, and Cohn<sup>25</sup> have used an instrument which is better suited to the study of dough texture than the various types of viscometers. With "isoviscous" doughs they found the same "viscosity" minimum, a little on the acid side of pH 5 which they discovered for gluten (see above), clear evidence that the texture of dough is dependent in the main upon the gluten. They conclude that the point of minimum viscosity is also the point at which dough is best baked, for it is the most favorable reaction for the rising of dough. Jessen-Hansen has found about pH 5 to be the best hydrogen ion concentration to give a dough when

<sup>46</sup> NEUMANN, M. P.: "Brot, Getreide und Brot," Berlin, 1914, p. 287.

<sup>47</sup> OSTWALD, Wo.: Beiträge zur Kolloidchemie des Brotes. I. Ueber kollidchemische Problem bei der Brotbereitung, *Kolloid-Z.*, **25** (1919), 26.

<sup>48</sup> GORTNER, R. A. and SHARP, P. F.: The physico-chemical properties of strong and weak flours. III. Viscosity as a measure of hydration capacity and the relation of the hydrogen ion concentration to imbibition in the different acids, *J. Phys. Chem.*, **27** (1923), 481.

<sup>49</sup> BINGHAM, E. C.: "Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922, p. 922.

freshly made. Salts, especially magnesium and sodium sulfate, in small amounts were found to diminish "viscosity," while with increasing concentration the reverse was the case. However, the effect of salts varies with the hydrogen ion concentration. At a more acid range of reaction, sodium chloride greatly depresses viscosity, while calcium chloride has its effect in a less acid range. The great effect of sulfates, however, may be recognized over a wide range of reaction.<sup>25</sup>

H. Lüers and Wo. Ostwald<sup>24</sup> studied the viscosity of dough solutions containing up to 20 per cent of flour by means of a Wm. Ostwald viscometer of wide bore. The viscosity increased rapidly with the concentration, but diminished slowly on standing. Only in the more concentrated solutions was there a slight increase of viscosity shortly after preparation. Addition of acid increased the viscosity, but sodium chloride decreased it.

Gortner and Sharp,<sup>48</sup> using the MacMichael viscometer, studied the behavior of 25 per cent flour suspensions when acid was added. All acids used, except metaphosphoric, increase viscosity. Sulfuric acid is least effective. All except some "weak" organic acids produce a distinct viscosity maximum. These maxima lie at higher levels for strong than for weak flours. The hydrogen ion concentration at the maxima is in the neighborhood of pH 3, but it is not the same for all acids. Neutral salts in 0.01 N concentration were found to lessen the viscosity rise caused by acids. The chlorides of potassium, magnesium, and sodium inhibit to about the same degree but less so than the sulfates of magnesium and potassium or calcium chloride. When the soluble electrolytes were removed from the flour by elutriation with water, the viscosity maxima were much higher, especially in the case of flours of high ash content, and the effects of the different acids became more nearly similar. However, the differences between different glens did not disappear; and the pH at which each acid produced the maximum viscosity was not changed. With alkali added in place of acid, the maxima were recorded at pH 11.0 and the suspensions were much more viscous than in the case of addition of acid. These alkali maxima were also different for different flours, and sodium hydrate had a far greater effect than barium hydrate. By long-continued elutriation of flour with water, nearly all the gliadin was removed.

The viscosity values obtained by adding lactic acid, which must have been due to glutenin, were much increased and were reached almost instantly. Magnesium sulfate depressed the values, more so than magnesium chloride.<sup>15</sup>

In general, it may be said that the physical properties of dough are affected in much the same way as gluten by the same agents. Given sufficient information about a flour, much can be deduced concerning its behavior. Flour may be regarded as a coarsely dispersed dry gel powder. When it is doughed, the dry gluten gel particles imbibe water to form an emulsion colloid in which is imbedded a suspensoid colloid, the starch granules. The rate of imbibition and the physical properties of the mass resulting from the imbibition, the dough, will depend upon the character of the dry gluten gel, of the reaction, and of the electrolytes. The changes which take place during fermentation in this emulsion colloid holding the suspensoid starch result from the development of acid by the ferment, from the action of the amylolytic and proteolytic enzymes, from the action of phytase which hydrolyzes phytin—to mention a few of the factors. The proteolytic enzyme will, by hydrolysis, tend to ruin the gluten. Its action must not proceed too far before the dough is ripe for the oven. The amylolytic enzyme furnishes fermentable carbohydrate for the formation of carbon dioxide gas and other acid. The enzyme must be present in sufficient quantity. Otherwise, not enough gas or acid may be formed to give the finished dough the proper texture before the proteolytic enzymes ruin the gluten. The phytase changes the buffer value of a dough.<sup>50</sup> If there is not enough gluten, the dough will tend to be too slack; if there is too much, it will be too stiff to permit of proper expansion. If there is too much buffering salt, fermentation will have difficulty in developing the optimum acidity. Too low acidity will not permit enzymes and ferments to act optimally. In short, the strength of a flour and the behavior of dough during fermentation are the resultant of many factors.

**Baking.**—At the end of fermentation the dough has a foam structure, because innumerable bubbles filled with fermentation gases are trapped in it. The walls surrounding the bubbles con-

<sup>50</sup> BAILEY, C. H. and SHERWOOD, R. C.: The march of hydrogen-ion concentration in bread doughs, *Ind. Eng. Chem.*, **15** (1923), 624.



sist, in the main, of the emulsion colloid gluten in which the suspensoid starch is imbedded. In the oven the bubbles expand. The bubble walls must be strong and distensible enough to prevent escape of gas before they become rigid by coagulation of the gluten proteins. The rate of coagulation is, therefore, important. Perhaps it is influenced by the reaction and the presence of electrolytes, for it has been shown that both greatly modify the heat coagulation of proteins.<sup>51,52</sup> The net result of the baking process is the fixation of the foam structure of the dough and the exchange of rôles between protein and starch. The emulsoid protein becomes a suspensoid by coagulation; the suspensoid starch becomes changed, in part, to an emulsoid gel by gelatinization. The result is that the plastic properties of the walls of the cells in the dough become changed so that, in bread, they are elastic rather than plastic.

**Bread.**—Even in the finished bread, colloid chemical phenomena continue. It is extremely probable that the growing stale of bread crumb is not the result—at any rate in its early stages—of loss of water, but of changes in the starch gel. It is probable that either this gel by syneresis separates a serum<sup>47</sup> or else undergoes reversion, so that a part of the starch separates from the gel, *i.e.*, changes from the emulsoid to the suspensoid state.<sup>23</sup>

**Practical Considerations.**—If all this be true, the majority—though by no means all—of the factors determining flour quality should be amenable to control, so that the practical baker should be in a position to emancipate himself from dependence upon a supply of very definite kinds of flour. For example, hydrogen ion concentration can be adjusted at least in two different ways. One is the obvious way of adjusting the acidity of the dough at the beginning. The other is to control the amount of acid produced during fermentation. This, in turn, may be done in various ways, but the simplest is to vary the length of the fermentation period. Methods such as these will make possible the baking of equally good bread from a larger variety of flours than is now

<sup>51</sup> CHICK, H. and MARTIN, C. H.: Die Hitzekoagulation der Eiweisskörper, *Kolloidchem. Beihefte*, **5** (1913), 49.

<sup>52</sup> SÖRENSEN, S. P. L. and JÜRGENSEN, E.: Sur la coagulation des substances protéiques par chauffage, *Compt.-rend. trav. lab. Carlsberg*, **10** (1911), 1.



commercially practiced, though it is not to be expected that good bread can be made from every flour. All this is being recognized by practical men today. Indeed, Weaver and Goldtrap<sup>53</sup> have suggested the substitution of the terms "flour of long fermentation period" and "flour of short fermentation period" for the terms "strong flour" and "weak flour." Moreover, by properly adjusting the amount of water in doughing and the length of the fermentation, Weaver and Goldtrap were able to produce bread of very nearly the same specific volume from a large variety of flours, both hard and soft.

The economic significance of these developments must in time prove tremendous. It is by no means improbable that the large premiums now paid for strong wheats will disappear, because such wheats will no longer be so eagerly sought as they are today. That time, if it comes, will change profoundly the wheat map of the world.

## RYE

**Proteins.**—The proteins of rye are very similar to those of wheat. Rye gliadin was formerly considered identical with that of wheat, but it is most certainly different, for its specific rotation is greater (T. B. Osborne<sup>7</sup>) and its behavior as a colloid different.<sup>13</sup> Groh and Friedl<sup>13</sup> believed rye to contain more than one prolamins. Lüers<sup>5</sup> studied the viscosity in the presence of acids, alkalies, and salts of rye gliadin suspensions prepared by the dilution of alcoholic solutions. In general, the two gliadins behaved in the same way, except that in every case the rye gliadin solutions were somewhat less viscous. They showed the same maxima and minima at practically the same points. The data, when charted, gave curves nearly parallel with, but at a distinctly lower level than the wheat gliadin curves. Lüers attributed the lesser viscosity of the rye gliadin solutions to the presence of impurities, and regarded his observations as supporting the view originally expressed by Osborne that wheat and rye gliadin are identical, apparently in ignorance of the fact that Osborne himself had long before abandoned this opinion.

Rye flour contains a glutelin insoluble in water, salt solutions, or alcohol of any strength. It is soluble in dilute acid and alkali

<sup>53</sup> Flour strength, *J. Am. Assoc. Cereal Chem.*, **7** (1922), 115.

but has not been prepared in a sufficiently pure state to make possible the exact determination of its properties.

In general, the proteins of rye are more readily soluble in aqueous media than those of wheat; and they do not show the same swelling phenomena, as evidenced by the fact that from rye nothing of the character of gluten can be obtained. Rye flour yields a short, only slightly elastic, dough which is almost soapy to the touch and cannot become so light and porous during fermentation as wheaten dough. The water absorption as measured by the dough yield is less, as well as the bread yield. It is commonly stated that, if a small amount of rye flour be mixed with wheat flour, and gluten be washed from the mixture, more is obtained than corresponds to the gluten in the wheat flour. As the proportion of rye flour is increased, less and less gluten, it is claimed, can be washed out, until, with about 35 parts of rye flour, no gluten at all can be obtained.<sup>54</sup> This statement is probably wrong in so far as the alleged increase of gluten yield through addition of small amounts of rye flour is concerned, for Arpin, Cottin, and Lucas,<sup>54</sup> using a wheat flour with 24.60 per cent of moist gluten, got less than the theoretical amount of gluten with the addition of as little as 6 per cent of rye flour. The figures given by Neumann, employing wheat flour with 35.2 per cent of moist gluten, which are supposed to show increase in gluten yield, lie well within the limits of error of the method. Apparently, as is to be expected, the unfavorable effect of rye is somewhat less in the case of wheat flours with high gluten content than in the case of those with low ones. Rice flour, according to Arpin, Cottin, and Lucas, has no such adverse effect as rye flour. One might, therefore, suspect that there are present in rye flour factors which inhibit gluten formation. This has, in fact, been assumed by von Fenyvessy,<sup>55</sup> because he found that the addition of glutenin from wheat to rye flour does not result in gluten formation. This and the fact that the addition of rye flour to wheat flour reduces the gluten yield progressively

<sup>54</sup> *Essai des farines au Laboratoire du Ministère du Commerce français. Bericht über den III Internationalen Congress für Angewandte Chemie, Wien, 2* (1898), 177.

<sup>55</sup> *Über den Einfluss einiger vegetabilischen Proteide auf den Weizenkleber, Z. Nahr. Genussm., 21* (1911), 658.

to zero led von Fenyvessy to reject Osborne's suggestion that no gluten can be obtained from rye because it contains no glutenin. On the other hand, as first shown by Osborne, the addition of pure rye gliadin to wheat flour increases proportionately the gluten yield and its distensibility exactly as does wheat gliadin. The argument of von Fenyvessy is not wholly conclusive, for he fails to state whether or not the glutenin added to the rye flour was denatured. It was probably prepared by extracting gluten with alcohol to remove gliadin. Alcohol, however, denatures glutenin.<sup>15</sup>

Lüers and Ostwald found rye flour suspensions in concentrations up to 20 per cent to be enormously more viscous than similar wheat flour suspensions. To what extent the viscosity is dependent upon the carbohydrate gum found in rye flour and soluble in salt solution has, apparently, not been determined. On standing, the viscosity of the rye dough suspensions increases greatly. They are relatively insensitive to acids. With increasing addition of acid, the viscosity may diminish somewhat. Addition of sodium chloride lowers the viscosity. Hard bicarbonate water increases the viscosity as compared with distilled water. Calcium sulfate water lowers it.

**Starch.**—Rye flour improves on aging, but to a lesser degree than wheat flour. It averages much more easily and is more perishable.

Rye starch granules gelatinize, according to Lippman, at 50° to 55°; according to Lintner, at 55° to 80°, and according to Reichert,<sup>40</sup> at 61° to 62°. Rye starch gelatinizes more easily than wheat starch<sup>56</sup> and is more easily attacked by diastase in the ungelatinized state.<sup>46</sup> When gelatinized, it is more viscous than wheat starch.<sup>24</sup>

The carbohydrate gum of rye does not seem to have been studied.

## BARLEY

The albumin (leucosin), the globulin (edestin), and the proteose of barley are very similar to those of wheat and rye. The pro-

<sup>56</sup> WEINWURM, S.: Ueber eine qualitative und quantitative Bestimmung von Weizenmehl im Roggenmehl, *Z. Nahr. Genussm.*, 1 (1898), 98.

lamin, hordein, is distinctly different, though its solubilities and many of its properties are similar to those of gliadin. Osborne estimated its minimum molecular weight to be 14,880.<sup>3</sup> The glutenin of barley,—the water, salt solution, and alcohol insoluble protein,—has never been obtained in a state of purity because of the presence in barley of considerable carbohydrate gum, which is soluble in dilute aqueous alkali. The proteins of malt have been found to be quite different from those of the dormant barley seed.

Little is known concerning the colloid properties of barley constituents, since nearly all the work upon them has been done from the viewpoint of the brewer. Landenberger and Morse<sup>57</sup> found that a pH of 5.0 and a 2 per cent salt content of the dough are the optimum conditions for the production of yeast-leavened bread from barley flour. Gluten cannot be obtained from barley. Barley starch gelatinizes at 61°.<sup>40</sup>

## MAIZE

Maize seems to contain three globulins, a little proteose, a glutelin, and a prolamin, zein. Corn flour contains little or no albumin. The glutelin has not yet been characterized satisfactorily.

**Zein.**—Zein is insoluble in 0.5 per cent sodium carbonate and in 0.2 per cent hydrochloric acid. It dissolves, without change, in 0.1 to 2.0 per cent potassium hydrate, and is freely soluble in stronger alcohol than the prolamins of wheat, rye, or barley. It is precipitated out of its solutions in alcohol by a lesser degree of dilution with water than are these other prolamins. Heat does not change it when in solution in strong alcohol, but it is coagulated in weaker alcohol. It is so soluble in ordinary commercial alcohol (92 per cent) that thick sirups may be obtained. Alcoholic solutions, on evaporation, form transparent films like collodion. It is quite insoluble in water and in absolute alcohol. Solutions in alcohol gelatinize on standing and finally become stiff gels. The zein is then no longer soluble in alcohol. It is

<sup>57</sup> Barley bread, optimum reaction and salt effect, *Science* N. S., **48** (1918), 269.



soluble in other alcohols, such as methyl and propyl. It dissolves in glycerin at about 150°. Such solutions solidify at 20°, and the zein is not changed when heated to 200°. When warmed with crystalline phenol it dissolves unchanged. Glacial acetic acid also dissolves it unchanged. Galeotti and Giampalmo<sup>58</sup> have determined its solubilities in the following systems, alcohol-water, alcohol-water-xylol, alcohol-water-sulfuric ether, alcohol-water-petroleum ether, alcohol-water-chloroform, and alcohol-water-acetone. It was found insoluble in all pure solvents but soluble in mixtures. When in a mixture of water, alcohol, and a lipid solvent, two phases separate, the zein passing entirely into the alcohol-water phase. Osborne has estimated its minimum molecular weight as 15,993.<sup>3</sup>

**Starch.**—The temperature of gelatinization of corn starch, according to Dox and Roark,<sup>59</sup> is 64.1° to 71° and is different for different varieties. In Chinese waxy maize the endosperm is colored red with iodine, which has been assumed to be due to the presence of erythrodextrin,<sup>60</sup> but which more probably is due to the presence of a starch of the type found in glutinous rice. In 4 per cent suspension the viscosity of ordinary commercial cornstarch at 100° is 2.49 to 2.73, if water be unity.<sup>61</sup> Commercial cornstarch contains 0.11 per cent of mineral matter.<sup>41</sup>

## OATS

The prolamin of oats is more easily coagulated than the prolamins previously considered and otherwise differs much from them. The globulin may be crystallized. Whether it is the sole globulin present has not been settled. Concerning the alkali-soluble protein, not very much is known. Oats contain little if any albumin. Oat starch gelatinizes at 63°.<sup>59</sup>

<sup>58</sup> Ueber die Löslichkeitsverhältnisse des Zeins in verschiedenen Lösungsmitteln, *Kolloid-Z.*, **3** (1908), 118.

<sup>59</sup> The determination of gelatinization temperatures of starches by means of an electrically heated chamber on the microscope stage, *J. Am. Chem. Soc.*, **39** (1917), 742.

<sup>60</sup> WEATHERWAX, P.: A rare carbohydrate in waxy maize, *Genetics*, **7** (1923), 568.

<sup>61</sup> MACNIDER, G. M.: A method for determining the value of commercial starches for use in cotton mills, *J. Ind. Eng. Chem.*, **4** (1912), 417.

## RICE

Concerning the rice proteins, but little is known. A prolamin does not seem to be present. Rice starch gelatinizes at 74° to 75°. It occurs in two forms, that colored blue by iodine, found in common rice, and that colored red by iodine, found in glutinous rice. Tadokoro and Sato<sup>41</sup> have studied the colloidal properties of the two kinds of rice starch, using starches that had been freed from protein with 0.3 per cent sodium hydroxide solution. Common rice starch granules swell less in iodine, potassium iodide, calcium chloride, and hydrochloric acid, adsorb more iodine, and resist sulfuric acid more than glutinous starch. Boiled glutinous rice starch adsorbs less iodine and releases it more easily than common starch. Such pseudo-solutions of common rice starch are more easily coagulated by H-ion than those of glutinous rice starch. Glutinous rice starch is a better protective colloid than common rice starch. The viscosity of a 1 per cent pseudo-solution of common starch is 2.93 (water = 1); of glutinous rice starch, 10.57. The syneresis of starch pastes is more rapid in the case of common starch. Charcoal made from glutinous rice starch has a greater adsorption power than that from common rice starch. Tadokoro and Sato conclude that the two types of starches do not differ chemically, but only in the degree of polymerization.

## MILLETS

Kaffir corn (*Andropogon*) contains a prolamin, kafrin,<sup>62</sup> very similar to zein. Its other proteins have not been studied adequately. Sorghum starch gelatinizes at 68 to 70° and occurs in two varieties, a glutinous and a common one. According to Tadokoro and Sato,<sup>41</sup> the two varieties of millet starch differ from one another in much the same way as the two types of rice starch.

<sup>62</sup> JONES, D. B. and JOHNS, C. O.: The hydrolysis of kafrin, *J. Biol. Chem.*, **36** (1918), 323.

## CHAPTER XXVI

### FRUIT JELLIES

By

LESTER W. TARR

The adaptability of a fruit juice to jelly-making purposes depends upon its content of pectin and acid. Tart apples, sour gooseberries, the more acid varieties of plums, sour quinces, red currants, and hard, firm berries are excellent sources of fruit for jellies, because of the abundance of pectin and acid which they contain. Other fruits, of which sweet apples, pears, and peaches may be cited as examples, have an abundant supply of pectin but are unsatisfactory for jelly-making, because of their deficiency in acid. On the other hand, tomatoes and rhubarb are plentifully supplied with acid, but, in the case of these fruits, it is pectin which is deficient. It is essential, therefore, that fruit juices for jelly-making purposes contain appreciable amounts of both pectin and acid.

In addition to pectin and acid, sugar is a necessary constituent of all fruit jellies. It does not matter whether the sugar content of the fruit juice itself be appreciable or not, sugar is usually added in the jelly-making process. Either beet or cane sugar, and in many instances even glucose sirup, is employed as the source of this constituent.

The chemistry of fruit jelly formation is chiefly concerned, therefore, with pectin, acid, and sugar. These three necessary constituents and water form a rather definite equilibrium when jelly formation occurs. Time of boiling, temperature, salt concentration, and the like are also important considerations, but their importance rests more particularly upon the manner in which they affect the pectin, acid, and sugar.

## PECTIN

It is possible here to refer only to those researches on pectin bodies which appear to be of particular interest in the development of this chapter. More complete reviews of the literature and descriptions of pectins have been made by von Lipmann,<sup>1</sup> Tollens,<sup>2</sup> Herbert,<sup>3</sup> Mangin,<sup>4</sup> and by Bigelow, Gore, and Howard.<sup>5</sup>

Pectins, or jelly-forming vegetable matters, were reported in fruit juices in 1833 by Braconnot<sup>6</sup> and were spoken of as the jelly-forming substances of fruit jellies. He also found them widely distributed in nature in rinds, in leaves and stems, as well as in many root-growing crops, such as turnips, carrots, and beets. Furthermore, Braconnot pointed out that pectin can be precipitated by alcohol, by various metallic salts, and by sugar.

Frémy<sup>7</sup> made an important contribution in 1840, in which he stated that pectin is present in unripe fruit mainly in an insoluble form as pectose. By treating with inorganic or organic acids with heat, pectose goes into solution as pectin. He suggested that pectose might be a calcium compound of pectin.

Frémy also discussed the changes which occurred in the cell wall as fruits ripen. Working with currants, he observed that the cell wall became thinner and the fruit less acid as ripening occurred, until at maturity the previously opaque cell walls had swollen and become transparent. The slender cell walls often burst or opened themselves so widely that the cell sap pressed out. This very acid sap came in contact with the outer substance and converted it into a mucilaginous, water-soluble compound, namely, into pectin and, possibly, into sugar.

Pectin is described by Frémy as existing according to the manner in which it is obtained as white, wool-like flakes, or as a tough, horny, somewhat elastic mass, or, occasionally, as a granular powder. It goes to a pasty consistency when soaked with water,

<sup>1</sup> "Chemie der Zuckerarten," 1895, pp. 924-936.

<sup>2</sup> "Handbuch der Kohlenhydrate," 1895, pp. 242-247.

<sup>3</sup> *Ann. Agron.*, **26** (1900), 34.

<sup>4</sup> *J. Bot.*, **5** (1891), 400; **6** (1892), 12.

<sup>5</sup> U. S. Dept. Agr., *Bull.* **94** (1905).

<sup>6</sup> *Ann. Chem. (Liebig)*, **5** (1833), 275.

<sup>7</sup> *J. Pharm. Chim.*, **26** (1840), 368.



and, upon the addition of more water, gives an opalescent, colloidal solution which rotates the plane of polarized light to the right. Pectin is insoluble in alcohol and ether, the precipitate which comes down upon the addition of alcohol being either gelatinous or flaky, according to the concentration of the alcohol. Acids do not coagulate a pectin solution, but many compounds of the heavy metals, such as the hydroxides of the alkaline earths, bring it down as a jelly; ammonium sulfate and magnesium sulfate give a flaky precipitate when introduced almost at the point of saturation.

It is interesting to observe the series of compounds which Frémy obtained from pectin. Parapectin was obtained by boiling pectin with water. It differed from pectin only in being precipitated by neutral lead acetate. Boiling pectin with dilute acid gave metapectin, which was like pectin and parapectin except that it was slightly acid and was precipitable by barium chloride. Continued boiling with acids gave parapectic acid, while the action of pectase, an enzyme, on pectin gave soluble pectosic acid, which gelatinized. Pectin was converted into pectic acid by the action of alkalies, the compound thus formed being soluble in alkalies but precipitated by acids. And, finally, by heating pectic acid to 200°C., pyropectic acid was formed.

The numerous pectin bodies described by Frémy represent only a few of the pectin bodies which have been identified and described by various investigators. It is unavoidable, therefore, that some confusion has ensued in comparing those of one investigator with those described by another. In general, pectin compounds are uncrystallizable bodies, which can be precipitated from their solutions by various reagents, and then appear very often in a colloidal, gelatinous condition. They are, however, very rapidly altered by the solutions used for their extraction. Frémy, Scheibler,<sup>8</sup> and Reichardt<sup>9</sup> considered them to be carbohydrates, allied to mucilages and gums. Mangin maintains that their reactions separate them from the carbohydrate group; when oxidized by dilute nitric acid, they give rise to mucic acid, whereas carbohydrates are converted into oxalic acid. They are insoluble in cupric ammonia, a reaction which Mangin em-

<sup>8</sup> *Ber.*, **1** (1868), 58, 108; **6** (1873), 612.

<sup>9</sup> *Ber.*, **8** (1875), 807.

ployed to show that they differ materially from the celluloses, although they have often been confounded with them.

The view of Frémy and others that they are related to carbohydrates found substantiation in the work of De Haas and Tollens.<sup>10</sup> As a result of analyses of pectins prepared from various sources, they showed that the ratio of hydrogen to oxygen in these bodies was nearly 1 to 8, as required by the carbohydrate formula, and that the pectin bodies which they studied contained no complex which gave rise to dextrose, but that complexes were present which yielded pentose sugars and galactose on hydrolyzing with mineral acids. They suggested later that pectin bodies may probably be regarded as glucosides.

One of the most interesting studies of the pectin bodies is that reported by Th. v. Fellenberg.<sup>11</sup> He divides the pectin bodies into three groups, namely, protopectin, pectin, and pectic acid. Protopectin, which corresponds to Frémy's pectose, he describes as the insoluble body which is obtained from unripe, and to a great extent also from ripe, fruits, but not in overripe, rotten fruits. He maintains, however, that protopectin is neither calcium pectinate nor a glucoside.

Pectin, or parapectin, he describes as the product obtained from fruit juices which forms a colloidal solution in water, but which is precipitated by alcohol. It is formed naturally from protopectin during the ripening process in fruits, it being possible, however, to effect the same transformation by hydrolysis. It is a reversible colloid. It is caused to swell by pouring water over it, finally going into complete solution, the solution thus obtained being opalescent with a turbid appearance. Under the ultramicroscope it is easy to distinguish existing particles of small dimensions in lively movement. Inspecting the jelly form with the ultramicroscope, streaks and shreds are discernible which clearly are held together by submicrons. Fellenberg states that pectin can be precipitated by copper sulfate, lead nitrate, and neutral and basic lead acetate. It is not precipitated by silver nitrate, mercurous chloride, cobalt nitrate, nickel sulfate, ferrous sulfate, zinc sulfate, manganese chloride, calcium chloride strontium chloride, barium chloride, nor the alkali salts.

<sup>10</sup> *Ann. Chem.* (Liebig), **286** (1895), 278.

<sup>11</sup> *Biochem. Z.*, **85** (1918), 118.

Fellenberg describes pectic acid as a very weak acid, which may be prepared by treating pectin with dilute sodium hydroxide and then with hydrochloric acid, filtering, washing with alcohol and ether, and drying. Pectic acid is very sensitive to the action of electrolytes.

The jellying properties of these three pectin bodies are quite distinctive. Protopectin itself does not form a jelly when cooked with sugar and pectin-free fruit juice. Pectin, however, is the substance to which the actual jellying of fruit juices is due. Pectic acid does not form a jelly with sugar and pectin-free juice, except when the enzyme, pectase, is present.

Fellenberg bases the action of the various pectin bodies on the methoxy groups that they contain. He states that protopectin upon hydrolysis yields pectin, which is considered to be an ester of pectic acid containing 8 methoxy groups. These methoxy groups can be split off gradually, the completely demethoxylated compound being pectic acid. Pectin is, therefore, the methyl ester of pectic acid. The transformation from pectin to pectic acid does not have to be complete, however. There can be a gradual splitting off of methoxy groups, resulting in the formation of a whole series of compounds of different methoxy contents. Frémy's pectin compounds are thus explained by Fellenberg as being derived by the gradual transformation of pectin through the loss of methoxy groups. As methoxy groups are split off, acid groups are attached. The more acid groups there are in the pectin molecule, the more easily precipitation is accomplished by metallic salts. This accounts for the sensitivity of pectic acid to precipitation by metallic salts as contrasted with pectin itself.

Fresh, barely ripe fruit is said to contain protopectin and a very little pectin, with no pectic acid or methyl alcohol. In rotten fruit the protopectin has disappeared, pectin is still present, and pectic acid and methyl alcohol exist in excess.

If the extraction of pectin from fruit is now given consideration, it will be recalled that pectin is present largely in the pulp of fruits, and not in the juice. Such portions of fruits as the skins of apples and the inner rinds of oranges and lemons are excellent sources of pectin. The entire fruit is used, therefore, for jelly-making purposes. Hard fruits are usually cut into pieces, covered

with water, and cooked until the tissues are soft. The same treatment is given in the case of soft fruits except that no water, or little water, need be added. It is economical, of course, to extract with as little added water as possible. At the end of the cooking period the liquid is allowed to drain from the pulp. If the pulp employed be that of a good jellying fruit, such as red currants, crab apples, or grapes, it can be treated again with water and subjected to a second and even to a third extraction.

The question of the method of extraction has come in for some investigation. Johnstin and Denton<sup>12</sup> extracted orange pectin by the open-kettle method and also by the autoclave method, in which pressure is used. Their data are presented in Table I.

TABLE I.—RESULTS WITH ORANGE PECTIN EXTRACTS PREPARED IN OPEN KETTLE AND AUTOCLAVE

Method	Alcohol precipitate, per cent	Acid in extract (calcd. as citric), per cent	Sugar in jelly, grams	Extract used in making jelly, grams	Grams of jelly per gram of extract	Grams of jelly per gram of peel
Open kettle, distilled water...	0.347	0.070	84	70	2.0	5.2
Open kettle, 0.1 N acid.....	0.890	1.900	84	27	5.2	13.7
Autoclave, 5 lb., 30 min., distilled water.....	0.565	0.057	84	90	1.5	3.9
Autoclave, 5 lb., 30 min., 0.1 N acid.....	0.960	1.270	84	60	2.3	6.0
Autoclave, 20 lb., 30 min., distilled water.....	1.690	0.120	84	90	No jelly	
Autoclave, 20 lb., 30 min., 0.1 N acid.....	1.770	1.520	84	70	No jelly	

Johnstin and Denton state that the use of pressure in the autoclave served to increase the pectin yield, yet the pectin prepared by this method did not have as great jellying power as comparable extracts obtained by open-kettle heating. They attribute this to the instability of the pectin bodies at the high temperatures existing in the autoclave.

In another series of experiments, Johnstin and Denton show the favorable effect of acid in extracting orange pectin. Extractions carried out with distilled water by the open-kettle method yielded 0.82 and 0.79 per cent of alcohol precipitate as contrasted with

<sup>12</sup> *Ind. Eng. Chem.*, **15** (1923), 778.



1.30 and 1.24 per cent respectively for extractions conducted in a similar manner with 0.1 N acid. They observed that the increase in alcohol precipitate obtained by acid extraction was accompanied by increase in jellying power, although not exactly in the same proportion. The presence of acid produced not only a larger quantity of pectin, but likewise a more effective pectin as regards jellying power. They observed also that lemon extracts, in general, contained a smaller percentage of alcohol precipitates; yet their jellying power averaged about 20 per cent higher than that of the average orange peel extracts. This was attributed to a difference in kind rather than in amount of pectin present.

Since the conditions for extracting pectin from ordinary fruit products necessitate boiling in acid solution, the question of pectin hydrolysis becomes of interest. That pectin can be hydrolyzed on sufficiently long boiling in acid solution was shown in the work of De Haas and Tollens.<sup>13</sup> They found that pectin was hydrolyzed upon being heated with 4 per cent  $H_2SO_4$ . Goldthwaite<sup>14</sup> also showed that, upon long-continued boiling, the acidity of ordinary fruit juices was sufficient to hydrolyze whatever pectin was present. It seems highly improbable, however, that the temperature and the short time usually required for extraction purposes would be sufficient to bring about any appreciable destruction of pectin. The higher temperatures employed in autoclave extraction might very well do so, as Johnstin and Denton have indicated.

Sucharipa<sup>15</sup> has recently supplied some interesting data which show the effect of temperature and pressure on the methoxy content of the extracted pectin. The white part, or albedo, of lemons was extracted with alcohol to remove resins, tannins, terpenes, and glucosides, after which it was extracted with cold distilled water. A fully methoxylated pectin (12.32 per cent methoxy) was obtained by this means, and since it could be extracted by cold distilled water, Sucharipa assumed that it must exist in a free state in the tissue. Extractions carried out with increasing temperatures and pressures produced pectins of decreas-

<sup>13</sup> *Ann. Chem.* (Liebig), **286**, 278.

<sup>14</sup> *J. Ind. Eng. Chem.*, **2** (1910), 457.

<sup>15</sup> *J. Assoc. Official Agr. Chem.*, **7** (1923), 57.

ing methoxy contents. When dissolved in water, these pectins showed marked differences in character; the greater the methoxy content, the greater was the viscosity observed. Their jellying power was also stated to be a direct function of their methoxy content.

Some idea of the complexity of the pectin bodies can be obtained from the brief discussion which has been presented here. Their identity is still an unsettled question, but the tremendous amount of research which is being focused in their direction holds forth brilliant promise for the future.

### ACID

An examination of the quantitative data on acidity as presented by several investigators shows that there must always be some acid with the pectin, sugar, and water before jelly formation can occur. When it comes to the question of how much acid is necessary, however, the variations are considerable.

Expressing the per cent of acid in the fruit juice as sulfuric acid, Goldthwaite<sup>16</sup> reports one instance in which a tough jelly was made from the pomace of Northern Spy apples, when the acidity was as low as 0.154 per cent. She reports having made good jelly from medium sour apples with an acidity of 0.257 per cent. Sour apples with an acidity of 0.860 per cent made excellent jelly, as did currants, blueberries, red raspberries, and blackberries, the acidities of which were 1.892, 1.332, 1.809, and 1.208 per cent respectively.

Cruess and McNair,<sup>17</sup> working largely with California fruits, state that juices containing less than 0.50 per cent acid as citric or tartaric (0.35 per cent sulfuric acid) did not usually form jelly. Working with a supposedly pure orange pectin, they determined that the optimum acidity of a good jellying fruit juice lay within the limits of 0.50 and 1.50 per cent acid, calculated as citric acid (0.35 and 1.05 per cent sulfuric acid).

Campbell<sup>18</sup> states that an acidity of 0.30 per cent, calculated as sulfuric acid, is necessary to produce a good-quality jelly, the

<sup>16</sup> *J. Ind. Eng. Chem.*, **1** (1909), 333; **2** (1910), 457.

<sup>17</sup> *J. Ind. Eng. Chem.*, **8** (1916), 417.

<sup>18</sup> *J. Ind. Eng. Chem.*, **12** (1920), 558.

minimum being 0.27 and the maximum 0.50 per cent. Apple juice was employed by Campbell in his experimental work.

And only recently Singh<sup>19</sup> has published an article on fruit jellies in which he states that, contrary to the claims made in the literature, it is possible to prepare jelly from a mixture of pectin, acid, sugar, and water, even if it is quite deficient in acid. Singh believes that there is a definite relation existing between the amount of acid present in fruit juice and the amount of sugar necessary to form a jelly. By varying the sugar content, he states that he has made jellies containing as little as 0.05 per cent citric acid (0.035 per cent sulfuric acid) and as much as 4.05 per cent (2.835 per cent sulfuric acid). The acidity is calculated as the total acid present in the finished jelly.

It seems quite impossible in view of these various data to correlate total acidity with jelly formation. Recently, however, Tarr<sup>20</sup> has endeavored to determine the effect of the strength of the acid on jelly formation, and here there appears to be a direct correlation.

Tarr employed a pectin stock solution which was prepared by diluting with distilled water one of the concentrated pectin products which could be purchased on the market. The stock solution thus prepared contained some acid, but not an amount sufficient to produce a jelly. The plan of procedure adopted consisted, therefore, of determining the amounts of various acids, ranging from weak to strong, which had to be added to a definite quantity of this stock solution (1) to produce a jelly and (2)

TABLE II.—DISSOCIATION CONSTANTS OF VARIOUS ACIDS EMPLOYED

Acid	Volume in liters	Dissociation constant
Sulfuric.....	10-40	$3.0 \times 10^{-2}$
Phosphoric.....	.....	$1.0 \times 10^{-2}$
Tartaric.....	16-2,048	$9.7 \times 10^{-4}$
Citric.....	16-2,048	$8.2 \times 10^{-4}$
Acetic.....	8-1,024	$1.8 \times 10^{-5}$

<sup>19</sup> *J. Ind. Eng. Chem.*, **14** (1922), 710.

<sup>20</sup> *Dela. Agr. Expt. Sta. Bull.* **134**, *Tech.* 2 (1923).

to produce the optimum jelly. Pectin and sugar were maintained constant in these experiments at 2 and 125 g. respectively. Determinations were made not only of the total acidity but also of the strength, or hydrogen ion concentration. The acids selected for the purpose with their dissociation constants are shown in Table II.

Expressed as cubic centimeters of 0.1 N acid, it was found that 8.5 cc. of sulfuric acid, 27.5 cc. of phosphoric acid, 22.7 cc. of tartaric acid, 52.9 cc. of citric acid, and 583.3 cc. of acetic acid

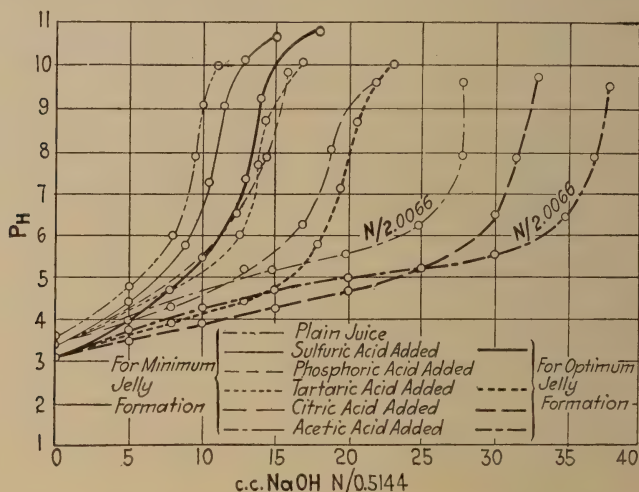


FIG. 1.—Electro-titration curves showing the amounts of the various acids necessary (a) to produce a jelly and (b) to produce the optimum jelly. Note that although the total acidity varies over a wide range, the hydrogen ion concentration is constant at pH 3.4 for the minimum point of jelly formation and pH 3.1 for the optimum point.

were the respective quantities of these various acids that had to be added to the original pectin stock solution to enable jelly formation to occur. Although these represent wide variations in total acidity, in all instances, the hydrogen ion concentration which resulted from the addition of these quantities of acids was exactly the same. This was pH 3.40 for the minimum point of jelly formation. The same relations were also maintained between the total and active acidities in the formation of the optimum jelly, the hydrogen ion concentration for this point being pH 3.1.



It is evident from these data that the strength of the acid, or hydrogen ion concentration, was the factor governing jelly formation, rather than the total acidity. A graphical representation of both the total and active acidity relations obtained is presented in Fig. 1.

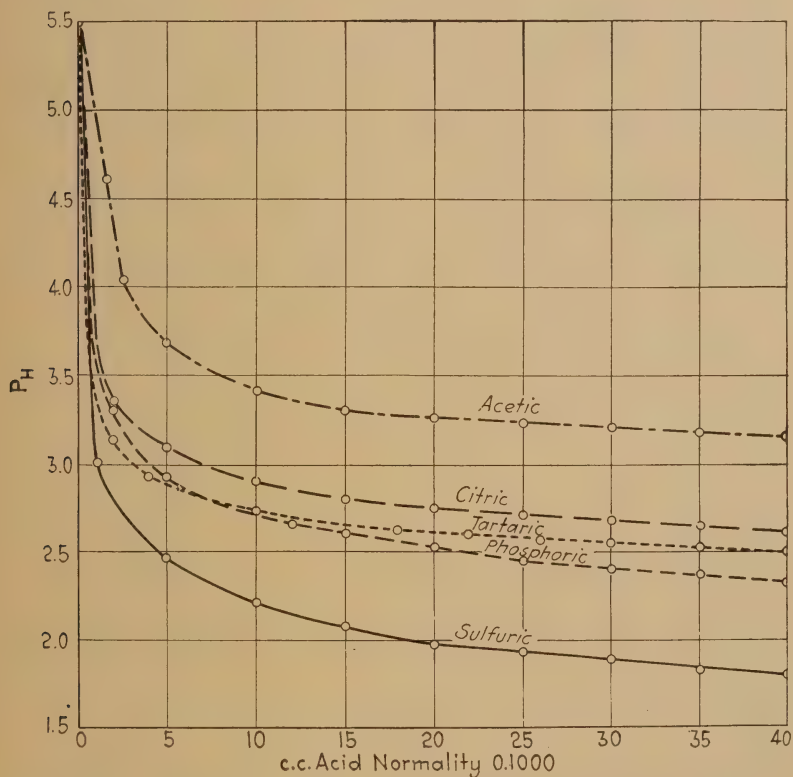


FIG. 2.—The effect of the addition of 0.1 N solutions of sulphuric, phosphoric, tartaric, citric, and acetic acids on 100 cc. of distilled water.

It is important to note in connection with these experiments that the character of the jelly was also directly affected by the hydrogen ion concentration. Whether a jelly was tender or firm did not depend upon the total amount of acid present, but entirely upon the concentration of hydrogen ions liberated by that acid.

The relationship which exists between total acidity and hydrogen ion concentration could be roughly established by means of the pectin stock solutions. For more accurate relationships, however, they were unsatisfactory because of the substances other than pectin which they contained, over which it was impossible to maintain control. A purified pectin was, therefore, prepared for further work.

The same acids employed in the preceding work were then added in small, accurately measured quantities to 100 cc. of distilled

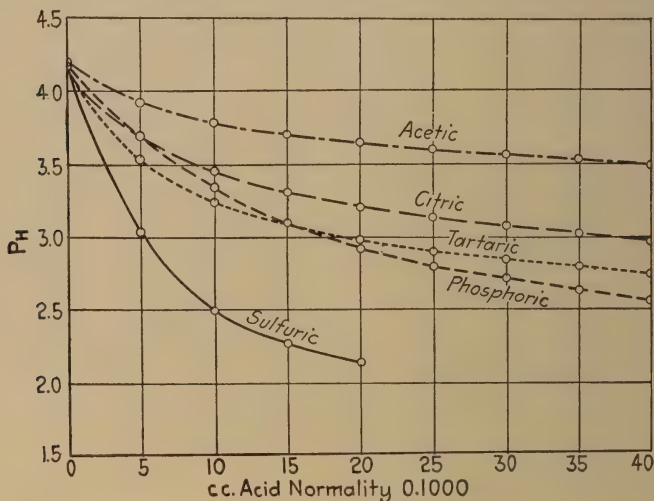


FIG. 3.—The effect of the additions of 0.1 *N* solutions of sulphuric, phosphoric, tartaric, citric, and acetic acids on 100 cc. of distilled water in which 1 g. of pectin is dissolved.

water and also to 100 cc. of distilled water in which 1 g. of the purified pectin was dissolved. Hydrogen ion concentration determinations were made in each case after each addition of acid. The results obtained are shown graphically in Figs. 2 and 3.

It will be observed upon examining the figures that the effect of acid on distilled water was entirely different from the effect of the same amount of acid on distilled water in which 1 g. of pectin was dissolved. The presence of the pectin decreased materially the dissociation of the various acids employed, thereby acting as a buffer.

It will also be observed that the effect of each acid was different. To produce a hydrogen ion concentration of pH 3.50, with the pectin dissolved in the water, required approximately 2.6 cc. of 0.1 *N* sulfuric acid, as compared with 5.5 cc. of 0.1 *N* tartaric acid, 7.5 cc. of 0.1 *N* phosphoric acid, or 8.5 cc. of 0.1 *N* citric acid. The total amount of acid required varied with the particular acid employed.

Furthermore, the relation found to exist between the acids and the effect which they produced on the hydrogen ion concentration with pectin present in the solution, was shown to be a purely stoichiometrical relation when based on the combining power of the acids. Loeb<sup>21</sup> has already shown this same relation-ship to exist between proteins and acids.

Weak dibasic or tribasic acids give off one hydrogen for combining purposes more readily than both or all three, depending entirely on the hydrogen ion concentration of the solution. At the hydrogen ion concentrations employed in these fruit jelly investigations—that is, below pH 4—there would be only one hydrogen liberated for combining purposes from such acids. With a strong dibasic acid like sulfuric acid, however, both hydrogens are held with so small an electrostatic force that, even at a hydrogen ion concentration of pH 3, or considerably below, the acid liberates both hydrogens. The action of sulfuric acid would, consequently, be similar to that of a strong monobasic acid like hydrochloric. It would follow, therefore, that, at the hydrogen ion concentration employed in these investigations, three times as many cubic centimeters of 0.1 *N* phosphoric acid should be required to produce a given pH as are required of 0.1 *N* sulfuric acid. And, in a similar manner, twice as many cubic centimeters of 0.1 *N* tartaric acid and three times as many cubic centimeters of 0.1 *N* citric acid should be required.

From the curves shown in Fig. 3, it will be observed that the relations just described were quite closely maintained. To produce a pH of 3.50 required approximately 2.6 cc. of 0.1 *N* sulfuric acid, while approximately 7.5 cc. of 0.1 *N* phosphoric acid were required to produce the same value. This relation maintained rather closely the 1: 3 ratio which should exist between

<sup>21</sup> "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., 1922. Cf. Chap. II, of this book (vol. 1).

these two acids. About 5.5 cc. of 0.1 *N* tartaric acid were required, as compared with the 2.6 cc. of 0.1 *N* sulfuric acid, a proportion approximating the 1:2 ratio which should exist. The relation is not an exact one, however, and with citric acid it will be observed that there was an even wider variation between the ratio which existed and the 1:3 ratio which it was indicated should exist; 10 cc. of 0.1 *N* citric acid were required as compared with the 2.6 cc. of 0.1 *N* sulfuric acid. About 40 cc. of 0.1 *N* acetic acid were required to produce a hydrogen ion concentration of pH 3.50.

The fact that the indicated ratios were not exactly maintained has already been pointed out. Furthermore, as the hydrogen ion concentration was increased, these relations became even more distant. This is exactly what would be expected, however, if compounds were formed with pectin and the acids which yielded ions common to the acids. Since the presence of pectin did materially decrease the dissociation of the acids, this suggests the formation either of some kind of pectin-acid compounds, or of compounds formed by the acids uniting with products split off from the pectin. The formation of such compounds with subsequent ionization to yield ions that were common to the acids could very well explain the phenomena observed.

It is interesting to observe that both Fellenberg and Tarr conceive of pectin-acid compounds. Fellenberg conceives of methoxy groups in the pectin molecule being replaced by acid groups, the presence of the latter groups making the pectin much more sensitive to precipitation by electrolytes. Tarr is inclined to consider pectin as having an isoelectric point, above which it unites with bases to form base-pectin compounds, and below which it unites with acids to form pectin-acid compounds.

Upon making jellies with the purified pectin, sugar, acid, and water, it was found that jelly formation occurred at approximately pH 3.46. The total acidity required to produce this hydrogen ion concentration varied, of course, with the particular acid employed. An interesting contrast was furnished between the total acidity required to enable jelly formation to occur with the purified pectin, and the total acidity necessary when the pectin stock solutions were employed. Although the same quantity of pectin (2 g.) was employed, considerable more acid was



required to form a jelly with the pectin stock solutions than was the case with the purified pectin (see Figs. 1 and 3). This was undoubtedly due to a difference in buffer effect. It emphasizes again the futility of employing total acidity as a measuring standard in studies concerning fruit jellies.

It has already been stated that, in addition to controlling the formation of the jelly, the hydrogen ion concentration also controlled the character of the jelly. Maintaining the sugar constant, a tender, delicate jelly was formed with the purified pectin when the hydrogen ion concentration was approximately pH 3.46. As the concentration increased, there was a corresponding increase in stability in the jelly until a pH of 3.1 to 3.2 was attained. Increasing the hydrogen ion concentration, much above pH 3.1 did not add noticeable firmness to the jelly. It did, however, result in syneresis, or a seeping out of the liquid contents of the jelly.

It seems reasonably certain, in view of these experimental results, that fruit jelly formation is largely controlled by the hydrogen ion concentration. Slight differences in the critical hydrogen ion concentration for different fruit juices can probably be explained on the basis of differences in salt concentration. The precipitation of pectin presents another instance, therefore, of the importance of hydrogen ion concentration in reactions dealing with colloids.

Considering now the acids that are most commonly stated to be present in fruit juices, malic, citric, and tartaric, the most efficient of the three for jelly-making purposes appears to be tartaric. Citric appears to be the least efficient; measured in terms of total acidity, about twice as much citric acid is necessary to make a jelly as is required of tartaric acid. This explains an interesting observation made by Goldthwaite<sup>22</sup> in 1909, to the effect that jellies made with tartaric acid were superior in texture and flavor to those made with citric acid. It explains also the wide differences which occur in the total acidities of the various fruit juices used for jelly-making purposes. A fruit juice having a high acid content with citric acid predominating would not have as great a hydrogen ion concentration as would a similar juice with tartaric acid predominating. From electrotitration curves, malic

<sup>22</sup> *J. Ind. Eng. Chem.*, 1 (1909), 333.

acid would appear to lie between citric and tartaric acids as regards efficiency for jelly-making purposes.

The relationships which exist between malic, citric, and tartaric acids are interestingly brought out in the electrotitration curves of these three acids, shown in Fig. 4. As the titration progresses with the formation of the sodium salts of the three acids, it is evident that the effect of the salt formation is greatest on citric acid, and least on tartaric acid, with malic acid lying between these two.

### SUGAR

Fruit jellies can be prepared without any sugar other than that contained in the fruit juice. Goldthwaite<sup>23</sup> prepared a jelly under such conditions and described it as being very tough. So-called cider jelly is also prepared by concentrating the juice from apples, no sugar being added. In general, however, the addition of sugar in the making of jelly determines the texture, appearance, and flavor of the jelly, as well as the quantity to be obtained.

The quantity of sugar to be added can be varied over rather wide limits and it will still be possible to produce jellies. It seems quite true, however, that a given quantity of fruit juice can be made into the most satisfactory jelly upon the addition of a rather definite quantity of sugar. Increasing the quantity of sugar above this amount produces increasing softness in the jelly, while decreasing the quantity increases the toughness of the jelly. Of course, the addition of too much sugar will result in a product that fails to hold together at all.

In spite of the fact that the quantity of sugar to be added can be varied over rather a wide range, the percentage of sugar existing in the finished jelly will be found to be reasonably constant. There is a very definite equilibrium existing between pectin, sugar, acid, and water when jelly formation occurs. Cruess and McNair<sup>24</sup> recognized this when they stated that, if sugar is added to a fruit juice and the mixture boiled down to a boiling point of 104 to 105°C., or to a concentration of 65 to 70

<sup>23</sup> *Loc. cit.*

<sup>24</sup> *J. Ind. Eng. Chem.*, **8** (1916), 417.

per cent dissolved solids, a jelly will form if the fruit juice is suited to the purpose.

Tarr<sup>25</sup> called attention to this equilibrium in his study of the acid factor in fruit jellies. Employing 100 g. of sugar, the jellies he obtained weighed 148 g. On the basis of the cane sugar added, the finished jelly contained 67.6 per cent sugar. Employing 125 g. of sugar, the finished jellies weighed 184 g., the percentage of sugar in this instance being 67.9 per cent. Although jellies were made employing two different weights of sugar, the percent-

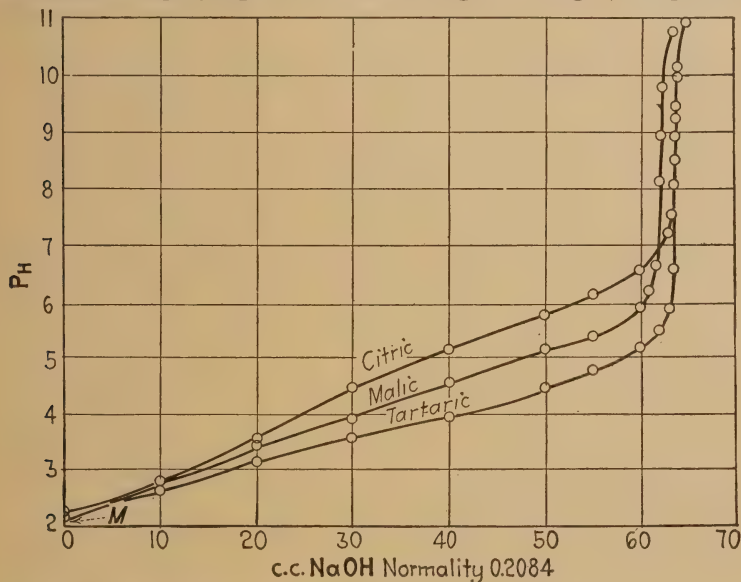


FIG. 4.—Electrotitration curves of 1 g. of tartaric acid and equivalent quantities of malic and citric acids. Due to an impurity in the malic acid, the quantity of this acid shown by the curve falls a little short of the calculated amount.

ages of sugar that existed in the finished jellies were nearly the same in both cases.

Tarr and Baker<sup>26</sup> investigated this equilibrium more carefully in their studies of the sugar factor in fruit jellies. In these studies the quantity of pectin stock solution which was necessary to provide 2 g. of pectin was carefully measured out. Jellies were made by adding varying quantities of sugar to the pectin, the

<sup>25</sup> Dela. Agr. Expt. Sta. *Bull.* 134, *Tech.* 2 (1923).

<sup>26</sup> Dela. Agr. Expt. Sta. *Bull.* 136, *Tech.* 3 (1924).

hydrogen ion concentration of the solution being carefully regulated. Some of the results obtained are presented in Table III.

TABLE III.—THE EFFECT OF SUGAR IN FRUIT JELLY FORMATION

Wt. pectin, grams	Wt. sugar, grams	pH	Wt. jelly, grams	Sugar in finished jelly, per cent
2	100	3.37	144.0	69.4
2	105	3.37	152.5	68.8
2	110	3.37	159.0	69.2
2	115	3.37	166.0	69.3
2	120	3.37	173.0	69.4
2	125	3.37	182.0	68.7
2	130	3.37	185.0	70.0
2	135	3.23	193.0	70.0
2	140	3.23	199.0	70.0
2	145	3.23	202.0	71.3
2	150	3.10	209.0	71.8
2	155	3.10	216.5	71.6
2	160	3.10	223.0	71.7
2	170	3.10	234.0	72.7
2	180	3.10	252.0	71.4

The data presented in Table III were arrived at by Tarr and Baker by making up jellies in the usual manner. The weight of the finished jelly was taken when that point was reached in the jelly-making process at which the solution showed a tendency to break from a silver spoon in a sheet form. This point could be judged with surprising accuracy after a little experience.

It is rather striking that, although the quantities of sugar employed varied over a range extending from 100 to 180 g., the percentages of sugars in the finished jellies, based on the original quantities of sugar employed, were constant within a reasonable limit of error. It will be observed that, as the hydrogen ion concentration was increased, the percentages of sugar in the finished jellies also increased slightly. Reference will be made to this point later.

Having established that a definite equilibrium existed between pectin, sugar, acid, and water, when jelly formation occurred, an effort was next made to determine the least quantity of sugar that



could be employed. Jellies were made as before, but, instead of concentrating until the jelly test was obtained, concentration was carried on until a definite weight was obtained. It was found that with 100 g. of sugar and 2 g. of pectin, 156 g. was the greatest weight of jelly that could be produced. Increasing the weight further would not enable a jelly to form which was stable enough to stand. Based on the original quantity of sugar employed, such a jelly contained approximately 64.1 per cent sugar. It was possible, therefore, with 100 g. of sugar to obtain a jelly ranging from 144 to 156 g. in weight, or from 69.4 to 64.1 per cent sugar content. Jellies formed with the lower percentage of sugar were very tender and weak, this being true regardless of the hydrogen ion concentration employed.

If the solubility of cane sugar in water is now considered, it will be found that at 20°C., 100 g. of water solution contain 67.09 g. of sugar.<sup>27</sup> In terms of cane sugar, therefore, a fruit jelly is more than a saturated solution of sugar. However, boiling the sugar with acid in the usual jelly-making process causes inversion of some of the cane sugar to glucose and fructose. This inversion with the consequent formation of glucose and fructose increases appreciably the solubility of cane sugar. According to the Bureau of Standards,<sup>28</sup> mixtures of maximum solubility at 20°C. contain 37.1 per cent cane sugar, 38.6 per cent invert sugar, and 24.3 per cent water. By inverting to obtain maximum solubility, therefore, as much as 73.77 per cent of cane sugar could be made soluble.

Tarr and Baker found (Table III) that, with a hydrogen ion concentration of pH 3.37, the "jell point" was attained with a concentration of slightly more than 69 per cent sugar in the finished jelly, calculated on the basis of the original sugar added. Increasing the hydrogen ion concentration to pH 3.23 increased the sugar in the finished jelly to 70 and 71 per cent. With a hydrogen ion concentration of pH 3.1, the sugar in the finished jelly was increased still further to 71 and 72 per cent. Increasing the hydrogen ion concentration caused greater inversion of cane sugar to glucose and fructose, thereby requiring more sugar to obtain a saturated solution. Tarr and Baker maintained,

<sup>27</sup> SEIDELL: "Solubilities of Inorganic and Organic Compounds," 1919.

<sup>28</sup> Personal communication.

therefore, that the precipitation of pectin in the form of a jelly occurred in the presence of a saturated, or nearly saturated, solution of sugar. Without doubt, substances other than sugar could be employed to produce the same result.

The extent to which the cane sugar was inverted at the different hydrogen ion concentrations employed is shown in Table IV.

TABLE IV.—THE INVERSION OF CANE SUGAR IN FRUIT JELLY FORMATION

Wt. pectin, grams	Wt. sugar, grams	pH	Wt. jelly, grams	Wt. invert sugar, grams	Wt. cane sugar, grams
2	100	3.37	145.0	27.97	72.03
2	125	3.37	181.0	28.77	96.23
2	150	3.37	217.5	29.36	120.64
2	100	3.23	145.0	35.09	64.91
2	125	3.23	181.0	41.21	83.79
2	150	3.23	217.5	40.53	109.47
2	100	3.10	145.0	46.00	54.00
2	125	3.10	181.0	50.45	74.55
2	150	3.10	217.5	56.71	93.29

Fruit jelly formation appears, therefore, to be a precipitation of the pectin in a saturated, or approximately saturated, solution of sugar. The quantity of sugar necessary to obtain this condition will undoubtedly vary, depending entirely upon the extent to which the substances present in the fruit juice affect the solubility of the sugar. The pectin precipitation appears to be controlled by the hydrogen ion concentration. The exact manner in which this precipitation is accomplished awaits further investigations, in which absolutely pure pectin is employed.

It is interesting to observe from Sucharipa's<sup>29</sup> studies that heat is not necessary to accomplish jelly formation. He prepared a jelly by mixing the ingredients in their proper amounts in the cold. The preparation of jellies under such conditions would seem to lend support to the views on jelly formation already expressed.

<sup>29</sup> *J. Assoc. Official Agr. Chem.*, 7 (1923), 57.

In concluding this presentation of the sugar factor in fruit jellies, attention should be called to the extent to which the capacity of pectin to hold sugar is increased by the hydrogen ion concentration. Employing 2 g. of pectin, Tarr and Baker<sup>30</sup> found that with a hydrogen ion concentration of pH 3.37, from 125 to 130 g. of sugar was the greatest quantity that could be added. More sugar than this resulted in a jelly that did not have sufficient stability to stand of its own accord. By increasing the hydrogen ion concentration to pH 3.23, the sugar-holding capacity of the pectin was increased to 145 to 150 g. Increasing the hydrogen ion concentration still further to pH 3.1 increased the sugar-holding capacity to as much as 170 to 180 g. These relations are really measures of jelly strength. They show that the jelly power of the pectin is appreciably affected by the hydrogen ion concentration. The same relation was expressed in the discussion of acidity, when it was stated that, with the sugar and pectin maintained constant, increase in hydrogen ion concentration resulted in increase in firmness of the jelly.

In explanation of the phenomena observed, Tarr conceives of fruit jellies as possessing, theoretically, the usual cellular structure of colloids of this type. From approximately pH 3.4 to 3.1, the colloid exists in the cell wall in a more or less viscous nature, entirely capable of holding the liquid contents of the jelly. The cell wall becomes firmer and firmer, however, as the hydrogen ion concentration is increased, thereby increasing the holding capacity of the cell wall. At hydrogen ion concentrations greater than approximately pH 3.1, the pectin becomes precipitated in the cell wall in a more or less granular form. The cell walls are no longer capable of retaining the liquid contents of jelly, and, therefore, syneresis, or a seeping out of the liquid contents of the jelly, occurs.

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## CHAPTER XXVII

### CELLULOSE AND ITS DERIVATIVES

By

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In view of the great importance of cellulose and its derivatives, it is surprising what a small amount of experimental study has been devoted to the elucidation of their colloidal behavior and properties. This is, in fact, the case to so marked a degree that it is necessary in many instances to rely largely upon analogy because the experimental evidence is lacking. This chapter is necessarily written, therefore, from this standpoint and is subject to revision, if necessary, as fast as the experimental results may become available.

Cellulose is widely distributed throughout the vegetable kingdom. It occurs in a comparatively pure form in cotton, and is also to be found in practically every form of vegetable life, inasmuch as it is the skeleton or framework upon which most plants are built. Cellulose, in other words, forms the cell walls.

It is met with in industry in four different forms.<sup>1</sup>

1. Seed hairs, of which cotton is the only representative.
2. Bast fibers, such as hemp, flax, manila, etc.
3. Fibers derived from whole stems, such as straw, esparto, or bamboo, and which are associated with various cells, and, accordingly, are not "fibers" in the strict sense of the word.
4. Fibers derived from wood.

This classification does not attempt to include the very wide variety of forms in which cellulose appears in the cell walls of different plants. It is intended to cover only those arrangements of cells which have been converted by natural processes into fibers, since these are the forms of cellulose which are of chief interest in industry.

<sup>1</sup> SUTERMEISTER: "The Chemistry of Pulp and Paper Making," 1920, p. 34 *et seq.*

## PHYSICAL STRUCTURE

The physical structure of cellulose varies widely and a detailed discussion of this property is hardly possible here. All modifications of cellulose, however, are essentially colloidal in character. The cellulose which has been most studied, and which is usually considered as the typical cellulose, is the cellulose from cotton. In considering certain of the chemical reactions of cellulose, it will be well to know a few things about the structure of the cotton fiber, since certain changes in this structure which can be followed under the microscope have been found to be of significance in interpreting some of the chemical transformations of cellulose. The cotton fiber<sup>2</sup> is essentially a flat, ribbon-like band, which is somewhat twisted and subjected to internal strain. It is made up of four parts: (1) the outside membrane, which is not soluble in Schweitzer's reagent; (2) true cellulose; (3) spiral fibers, all close to the outside membrane and which are not readily soluble in Schweitzer's reagent; (4) insoluble matter occupying the core of the fiber.

It seems probable that those portions other than the main bulk of the fiber are cellulose in a different colloidal state, possibly a different degree of dispersion. In other words, cotton fiber consists of a complex structure of cellulose in different physical states and contains, in addition, small amounts of fatty, protein, and mineral matter, partly in the central canal and partly dispersed throughout the fiber. Cellulose from wood is, at least in its raw state, a much more complex mixture and will be considered later.

**Formation and Lignification.**—It is generally considered that cellulose in plants is formed chemically from carbon dioxide, forming, first, formaldehyde, and this, in turn, passing step by step through six-carbon carbohydrates, which seem to combine by splitting off water and are finally converted into cellulose. Although the cellulose which forms the structure of plants may very well be the same chemical identity in different species, wide differences in physical properties are readily recognized. It has recently been suggested<sup>3</sup> that these differences may be

<sup>2</sup> HARRISON: *Trans. Nat. Assoc. Cotton Mfrs.*, **101** (1916), 201.

<sup>3</sup> WISLICENUS: *Kolloid-Z.*, **27** (1920), 209.

due to the variability of the lignin. This latter material is composed of the hydrosols of high molecular weight which are colloiddally dissolved in the formative or cambial sap and which are deposited by adsorption on the surface of the cellulose fibers. The variability of the lignin, which is held responsible for the differences in physical properties of the various kinds of wood, is attributed to the variability of the sap. It has been found that the amount of adsorbable material in the formative juices may vary from 6 to 30 per cent with the season of the year, and the maximum colloidal content coincides with the maximum lignification. While lignification depends mainly on adsorption, it is very probably followed by certain chemical reactions resulting in dehydration, toughening, aging, and the formation of complexes resembling cellulose in their colloidal properties.

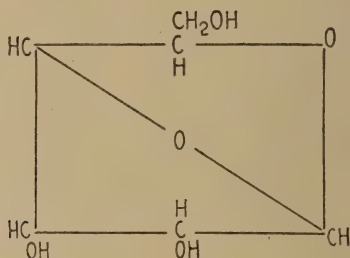
#### COMPOSITION AND CONSTITUTION

Although cellulose has been in practical use for centuries, it is only within a comparatively few years that any attention has been paid to the chemistry of the material itself or to the chemistry of the processes in which it is used. It is not surprising, therefore, that at the present time authorities are not agreed as to whether cellulose obtained from cotton is the same chemical individual as cellulose obtained from straw, or as cellulose obtained from different kinds of wood. A number of the leading authorities in this branch of chemistry have come out with the positive assertion that cellulose from all these sources is identical.<sup>4</sup> Other authorities question the statement and, unfortunately, the situation is somewhat complicated because of a lack of agreement on a definition of just what constitutes cellulose as obtained from wood. In other words, some investigators maintain that when cellulose obtained from such sources appears to be different from cotton cellulose it is merely because it is not pure and that if it were sufficiently purified it would be identical. Other schools, on the other hand, maintain that the differences are not due to impurities but that the "impurities" are really an integral part of the cellulose derived from such sources.

<sup>4</sup> HEUSER: *Z. angew. Chem.*, **34** (1921), 461; WISE and RUSSELL: *J. Ind. Eng. Chem.*, **14** (1922), 285; WISE: *Ibid.*, **15** (1923), 711.

It has been known for some time that the empirical composition of cellulose is  $C_6H_{10}O_5$  and that it is to be classed as a carbohydrate. It is only within the last few years, however, that we have had any idea of the arrangement of the atoms in the molecule, aside from the fact that there were three hydroxyl groups present. Thanks to the work of Irvine and his associates in Scotland, and the work of Hibbert in this country, we now have a fairly good conception of the constitution of the nucleus from which the cellulose molecule is built up. It is not possible to say exactly how many of these nuclei are present in the ordinary cellulose molecule, but at present it looks as if this number were three or four.

Hibbert<sup>5</sup> was the first to point out that, of the three hydroxyl groups present in cellulose, two are secondary and one is a primary alcohol group. The formula which he suggested is as follows:



Further evidence in favor of this formula has been contributed by Irvine and Hirst,<sup>6</sup> who have shown that cellulose is made up entirely of glucose residues and, further, that these residues are all alike.

#### ELECTRICAL PROPERTIES

In common with most materials in the colloidal condition, cellulose, when immersed in water, assumes an electrical charge, in this case a negative charge. It has been suggested<sup>7</sup> that this may

<sup>5</sup> HIBBERT: *J. Ind. Eng. Chem.*, **13** (1921), 256, 334; HIBBERT and HILL: *J. Am. Chem. Soc.*, **45** (1923), 734.

<sup>6</sup> *J. Chem. Soc.*, **121** (1922), 1585; **123** (1923), 518; *Chem. Trade J.*, **71** (1922), 291.

<sup>7</sup> MINOR: *Paper*, **25** (1919), 700; **26** (1920), 584.



be due to the existence of a positive residual valency in the cellulose molecule, which results in an adsorption of negative ions, leaving the cellulose negatively charged in relation to the solution. An illustration of this is seen in the fact that, when a very dilute solution of sodium chloride is filtered through clean cotton, the filtrate is found to be a dilute solution of hydrochloric acid. Similarly, if a very dilute sodium hydroxide solution is filtered through a similar medium, the filtrate is pure water.

**Adsorption.**—When treated with dilute aqueous acid or alkalis at room temperature, cellulose adsorbs the acid or alkali from the solution, accompanied by a very slight rise in temperature. It also readily adsorbs barium hydroxide as well as basic oxides from solutions of lead, zinc, copper, tin, aluminum, iron, and chromium salts.<sup>8</sup> Some investigators claim that at least part of the observed adsorptions are due to the non-cellulose material which is present as an impurity.<sup>9</sup> The question can hardly be regarded as settled, but there certainly seems to be evidence that cellulose itself does adsorb certain materials from solution, whether or not certain of the other adsorptions are due to non-cellulosic impurities.

### CHEMICAL CHARACTERISTICS

From the chemical standpoint, cellulose as it occurs in nature is composed of highly complex molecular groups which cannot be crystallized nor distilled without decomposition, and which are characterized by chemical inertness and colloid solubility. The property of cellulose on which its greatest usefulness depends is probably its general chemical inertness. Under certain conditions, however, as will be pointed out later, cellulose does react and it then behaves like an amphoteric compound exhibiting the properties of a weak acid and a still weaker base. In spite of its general inertness, however, an almost paradoxical behavior has

<sup>8</sup> See summary by HEUSER: *Cellulosechemie*, **1** (1920), 1; translated in *Paper*, **27**, No. 18, p. 17; No. 19, p. 15; No. 20, p. 22 (Jan., 1921).

<sup>9</sup> TINGLE: *J. Ind. Eng. Chem.*, **14** (1922), 198; SCHERINGA: *Pharm. Weekblad*, **57** (1920), 1289; GRIMM: *Xellstoff Papier*, **1** (1921), 7, 33; RONA and MICHAELIS: *Biochem. Z.*, **103** (1920), 19; BHATNAGAR: *J. Phys. Chem.*, **26** (1922), 61.

recently been noticed by Cross and Bevan, who found that two samples of cellulose, identical except for the fact that one had been boiled in distilled water for 2 hours and then dried, exhibited markedly different chemical characteristics. Indeed, there seems to be evidence that any treatment to which cellulose is subjected, either physical or chemical, modifies its chemical activity. From one point of view, of course, this merely emphasizes the colloidal nature of cellulose.

Next to its general inertness, the most important chemical characteristic of cellulose is the fact that it is an aliphatic alcohol and, as such, can be made to undergo certain of the reactions characteristic of such compounds, particularly esterification and the xanthate reaction. This alcoholic nature of cellulose is the property which makes possible nitrocellulose and its many applications, cellulose acetate, and the various varieties of artificial silk. The reactions leading to these materials will be considered later in this chapter.

**Hydration.**—So-called hydration of cellulose is observed when cellulose remains in contact with water for any length of time, particularly if, at the same time, it is mechanically agitated. In the process of paper making, for example, one of the objects of the treatment in the beater is to hydrate the cellulose. It is interesting to note in this connection that the degree of hydration of the cellulose in the beater seems to reach a maximum under certain conditions and then falls off.<sup>10</sup> When uncontaminated by hydrolysis, hydration appears to be essentially a swelling of the cellulose and an increase in its degree of dispersion.

The nature of the cellulose raw material has a bearing on the ease of hydration.<sup>11</sup> While coniferous woods may, as a rule, be readily hydrated by mechanical action in the presence of water, hard woods are not so susceptible to this treatment. If a little alkali is present in the water, however, hard woods may also be readily gelatinized by grinding.

In the examples of hydration just cited, the action is probably not purely that of hydration but is also accompanied by hydrolysis, which, in turn, leads to certain decomposition products. This will be taken up under "Hydrolysis."

<sup>10</sup> SCHWALBE: *Wochbl. Papierfabr.*, **54** (1923), 22.

<sup>11</sup> SCHORGER: *Ind. Eng. Chem.*, **15** (1923), 812.

**Mercerization.**—Mercerization may be regarded as a special case of hydration, since recent evidence seems to indicate that it is really only a case of increasing the degree of dispersion. When cellulose is treated with caustic soda solution, it swells. One theory<sup>12</sup> as to the reason for this swelling is that the cellulose, under these conditions, adsorbs hydroxyl ions from the solution forming adsorption compounds, accompanied by changes in physical state at certain concentrations of alkali. The swelling is to be attributed to the repulsive force acting between the adsorbed ions, forcing the cell walls farther apart. At the same time the sodium ions are held in close proximity to the adsorbed hydroxyl ions and thus form a second layer near the surface. As the swelling proceeds, the ions may tend to arrange themselves in such a way as to neutralize the original electrostatic repulsion, which would explain the fact that, finally, the swelling ceases to increase. The presence of salts would naturally be expected to have an effect on the swelling, either increasing it or decreasing it according to the nature of the salts present. At the same time that the swelling is taking place, an untwisting of the fiber is noticeable and a shortening of its length. The untwisting is probably to be accounted for on the ground that the strains in the original cotton fiber are distributed, partly at least, in spiral form.

Many colloidal substances react with iodine and give products of varied colors, the color combinations varying with the degree of dispersion. A low degree of dispersion gives a yellow color; as the degree of dispersion increases the color changes to orange, red, violet, to blue. By means of this test, mercerized cotton is shown to be cellulose in a more highly dispersed state than ordinary cellulose. This observation is confirmed by the ultra-microscope.

Mercerizing consists in allowing cellulose to swell under the action of an 18 to 25 per cent solution of caustic soda for from 10 to 30 minutes at a temperature not over 20°C. The product is then dried under tension. Under these conditions a luster is developed which has been attributed to the smoothness of the surface of the mercerized fiber as compared with the surface of unmercerized cotton, or cotton which has been mercerized and

<sup>12</sup> TOLMAN and STEARN: *J. Am. Chem. Soc.*, **40** (1918), 204.

not dried under tension. In addition to this smoother surface the mercerized cotton possesses a regular structure which is not possessed by untreated cotton or cotton treated with alkali and not dried under tension.

Mercerized cellulose, even after the complete removal of the alkali, is more hygroscopic than ordinary cellulose, has a greater absorptive capacity for dyes, and, in general, is more reactive. These properties seem to be due to the increased surface area formed as a result of the increased dispersion, rather than to any chemical change.

**Hydrolysis.**—When cellulose is acted upon by acids, a more or less complete hydrolysis takes place, depending on conditions. Outwardly, this change demonstrates itself in a physical weakening of the cellulose, often, though not always, accompanied by an increase in its affinity for basic dyes. The product is known as hydrocellulose and was originally considered to be a homogeneous chemical individual. It has recently been demonstrated, however, that hydrocellulose consists in reality of at least two materials, namely, unchanged cellulose and soluble degradation products of lower molecular weight. The hydrolysis does not stop at any intermediate step but proceeds gradually to the end product, glucose. In hydrocellulose we probably have not only unchanged cellulose and a little glucose, but all the intermediate products as well.

If hydrocellulose is examined under the microscope, it is found that the largest part of it is unchanged cellulose and, though the fibers are to a large extent broken, they still exist as fibrous fragments. The outer and inner walls of the fibers have been etched by the acid. They are no longer sharply defined against the hollow spaces but are rather swollen and indefinite. The decomposition products, however, are soluble in Fehling's solution, so that, if, after boiling in this solution, the cuprous oxide is dissolved out and the product thoroughly washed, the residue shows under the microscope the characteristic form of unchanged cellulose. The fiber structure is readily recognized and the hollow spaces are again sharply defined. They are, however, no longer smooth, as in untreated cellulose, but jagged. The decomposition products are also readily soluble in aqueous alkali.



While, therefore, hydrocellulose is still used as the name for the variable powder obtained from cellulose by treatment with dilute acid, the material thus designated is no longer considered as a chemical individual, but is rather to be looked upon as made up of an adsorbent part and an adsorbed part. The adsorbent part is the unchanged cellulose, whereas the adsorbed parts are the degradation products with an increased reducing power, and a lower molecular weight, which are produced by the action of the acid. They probably partake of the nature of dextrin and glucose.

**Action of the Beater in Paper Making.**—As has been suggested above, when cellulose is submitted to the action of the beater in paper making, two chemical changes take place. In the first place, there is hydration, and, in the second place, hydrolysis. The latter proceeds much more slowly than the former. It has, for example, been pointed out<sup>13</sup> that there is a big difference between pulp which has been hydrated by long beating and pulp which has been brought to the same degree of hydration by a short beating followed by cutting in the Jordan. When there is only a short time of beating, the effect on the cellulose is largely that of hydration; when there is long beating, we have both hydration and hydrolysis. The first step in the hydrolysis is the formation of mucilaginous, soluble dextrans. These are adsorbed by the cellulose to form hydrocellulose. They also seem to function as catalysts of the hydrolysis, as is indicated by the fact that pulps with a high copper number can be beaten to a "mucilage" easier than those with a low copper number. The formation of the "mucilage" seems to be due to the gradually increasing adsorption by the cellulose of the soluble dextrans, until the whole mass is finally converted to the characteristic physical conditions of the "mucilage."

Cellulose "mucilage" is probably a special form of hydrocellulose made up of an adsorbent part, cellulose, and an adsorbed part consisting of the degradation products of lower molecular weight. It has much greater water-absorbing powers than cellulose, has a greater affinity for dyes, and adsorbs metallic ions more readily than does pure cellulose.

<sup>13</sup> SCHWALBE: *Z. angew. Chem.*, **32** (1919), I, 355; MINOR: *J. Ind. Eng. Chem.*, **13** (1921), 131.

**Action of Sulfuric Acid—Parchment Paper.**—While the decomposition of cellulose by sulfuric acid has usually been referred to as a solution process, it has recently been pointed out<sup>13</sup> that it really is not solution but adsorption, followed by peptization and a subsequent entire alteration of atomic affinities. One of the earliest observations of the action of sulfuric acid on cellulose was in the manufacture of parchment paper. In this operation the first effect is the adsorption of sulfuric acid by the cellulose to form a series of adsorption compounds, accompanied by swelling and peptization. In making parchment, this process is stopped by plunging the product into water, which decomposes the sulfuric acid adsorption compounds and gives a gelatinous hydrate. It is probable that whatever concentration of sulfuric acid is used, a series of adsorption compounds is formed, accompanied by both hydration and hydrolysis, which result, respectively, in an increase in the reducing power of the cellulose and in molecular disintegration. If the aqueous solution of these adsorption compounds is boiled, glucose and sulfuric acid are produced. When wood cellulose is used, the reaction with sulfuric acid is more complicated, and yields furfural and condensation products of the latter.

**Action of Zinc Chloride—"Vulcanized Fiber."**—When cellulose is immersed in a concentrated aqueous solution of zinc chloride, swelling is also observed. In this case the swelling is supposed to be due to the adsorption of zinc oxide. That zinc oxide is adsorbed is proved by the fact that, when precipitated in water, the resulting cellulose hydrate retains 18 to 25 per cent zinc oxide, which is removable only by acid. It has been suggested<sup>13</sup> that the adsorbed zinc oxide or zinc hydroxide weakens the bonds which hold the colloid cellulose molecule together. In other words, a certain peptization is accomplished. In confirmation of this theory, it may be noted that sodium hydroxide does not effect the solution of normal cellulose, but does dissolve cellulose hydrate precipitated from its solution in zinc or copper compounds. After the initial swelling in zinc chloride solution, gentle heat is required to bring about final solution. If a hydrochloric acid solution of zinc chloride is used, the cellulose dissolves at room temperature, but the solution is then accompanied by a gradual molecular breakdown. The solution is

a rather unstable one, being broken up by mere dilution with water.

The treatment of cellulose with zinc chloride solution is the basis of the hard fiber or "vulcanized" fiber industry. In general, the process consists in passing paper, usually in four or five plies, through a cold or lukewarm solution of zinc chloride. This solution is a concentrated one, usually about 70° Bé. As it leaves the zinc chloride solution, the paper is passed through squeeze and calender rolls and is then washed by passing it continuously up and down over power-driven rolls through solutions which are gradually stepped down from 17° Bé. zinc chloride to pure water. When properly washed, there is no zinc in the finished paper. The sheets are combined to the desired thickness under hydraulic pressure. They are then dried and converted into the finished form.

**Cuprammonium Solutions.**—When treated with an ammoniacal solution of copper oxide, cellulose is rapidly attacked in the cold, forming a series of gelatinous hydrates, which pass into solution. The action is again probably due to the initial adsorption of copper oxide, and the explanation is probably the same as in the case of zinc chloride. The solutions are not very stable, being readily precipitated by alcohol or sodium chloride.

If the cellulose is allowed to remain in contact with the cuprammonium solution for a long time, some oxycellulose is formed and also a considerable quantity of nitrite. In other words, oxidation takes place slowly. As regards hydrolysis, cotton cellulose is not hydrolyzed by the process, but some forms of cellulose are.

The solubility of cellulose in cuprammonium solutions is the basis of one of the successful processes for the manufacture of artificial silk. This variety of silk is known as "Pauly" or "Glanzstoff" silk, and is usually made from cotton, generally in the form of linters.<sup>14</sup> The cotton is boiled with a dilute soda solution, washed, and bleached. It is next given a short beating in a Hollander and after being centrifuged is ready for solution. The cuprammonium solution is ordinarily prepared by covering copper turnings with 14 per cent aqua ammonia and blowing air through the mixture, which is maintained at a temperature below 4°C. About 250 lb. of cotton on the dry basis are dissolved

<sup>14</sup> WILSON, L. P.: *J. Soc. Chem. Ind.*, **36** (1917), 817.



in 2,500 lb. of solution, care being taken all the time to maintain a temperature below 5°C. This solution is then forced through very fine orifices into a liquid in which coagulation takes place. This liquid was at first 50 per cent sulfuric acid, but this has more recently been replaced by a 40 per cent caustic soda solution to which some glucose has been added for the purpose of reducing the copper. The thread as it comes from the coagulating bath is wound onto large glass bobbins and is then immersed in dilute acid, washed thoroughly, and finally dried at a temperature of about 50 to 60°C.

**Action of Thiocyanates.**—Somewhat similar to the action of zinc chloride solution is the effect of solutions of thiocyanates on cellulose. It has been found experimentally<sup>15</sup> that, in order to serve as a solvent for cellulose, a concentrated neutral aqueous solution of a neutral or acid salt must consist of a liquid hydrate which has a viscosity above a certain minimum and a positive heat of solution between certain well-defined limits. A concentrated solution of calcium thiocyanate, for example, is very viscous and dissolves cellulose. In order to dissolve bleached cotton or chemical wood pulp when heated to 80 to 100°C., a solution which has a boiling point between 135 and 150°C. is necessary. Solutions boiling above or below these limits are not solvents. The addition of from 2 to 4 g. of acetic acid per 100 cc. of solution facilitates the dissolving of the cellulose. When handled in the proper way, unsized paper can be parchmented with such solutions and mercerizing effects can be obtained on cotton.

**Oxidation—Oxycellulose.**—The name oxycellulose is applied to all products formed by the action of oxidizing agents on cellulose. As in the case of hydrocellulose, however, it is very doubtful whether the material thus designated is a homogeneous product. Oxycelluloses contain, in addition to unchanged cellulose, various decomposition products, depending upon the method used for their preparation. When cellulose is oxidized, the primary alcohol group is apparently converted to an aldehyde group and the product has a greater reducing power than the original material. The oxidation, however, is a gradual one, so that the reaction product contains some unchanged or very slightly changed cellulose, while the oxidation of another portion

<sup>15</sup> WILLIAMS: *J. Soc. Chem. Ind.*, **40** (1921), 221T.



may have proceeded far beyond oxycellulose. If the product is heated with 10 per cent sodium hydroxide, a part of it is dissolved and at the same time the insoluble residue is found to possess little or no reducing power. It seems probable, therefore, that the true oxycellulose has been dissolved, leaving unchanged cellulose. Even the part soluble in sodium hydroxide, however, is not homogeneous, since only part of it can be reprecipitated with acid. There is evidence<sup>16</sup> for believing that a part of the so-called oxycellulose is a dibasic aldehyde-carboxylic acid derived from cellubionic acid. From the colloidal point of view, oxycellulose may be considered as a peptized form of cellulose in which the adsorbed substances have greater reducing power than those present in hydrocellulose.

It might be said that there are as many methods of preparing oxycellulose as there are oxidizing agents. Even atmospheric oxygen under the proper conditions will oxidize cellulose. For example, bleached cotton, when heated in air in a sealed tube at 80 to 100°C. for several weeks, absorbs practically all of the oxygen in the tube. This is accompanied by the formation of small amounts of acetic and formic acid and a marked decrease in strength. Unless suitable precautions are taken, oxycellulose is encountered during the usual boiling of cotton textiles with caustic soda solution. If air is present, the oxygen in it will change the cellulose to oxycellulose.

The oxidation of cellulose is guarded against as much as possible in all the practical uses of cellulose, because it results in a weakening and finally a complete disintegration of the fiber structure.

**Viscose.**—There is a well-known reaction by which carbon disulfide reacts with alcoholic sodium hydroxide to yield a xanthate having the general formula  $(\text{XO})\text{C}:\text{S}(\text{SNa})$ , where X represents the hydrocarbon radical of an alcohol. Cellulose is enough of an alcohol to respond to this reaction. In carrying out the reaction in practice, cellulose is soaked in an aqueous sodium hydroxide solution of about 18 to 20 per cent strength for several hours. This is preferably done out of contact with the atmosphere to avoid oxycellulose formation. The surplus liquid is then removed in a centrifuge or press, the cellulose usually

<sup>16</sup> HEUSER and STÖCKIGT: *Cellulosechemie*, **3** (1922), 61.

retaining about three times its weight of solution. It is then broken up into small pieces and, after suitable aging, is treated with carbon disulfide in a closed container, the amount of carbon disulfide used being one-half the weight of the original cellulose. After standing several hours in a cool place, water is added to the mixture, and the solid is allowed to swell. On stirring, a smooth colloidal solution may be obtained which is yellow in color, due to the presence of colored by-products. It consists essentially of cellulose xanthate. The cellulose xanthate may be precipitated with alcohol or brine and redissolved in water. One or two such precipitations yield a product dissolving in water to a colorless solution.

From the standpoint of colloid chemistry, the process proceeds in several distinct steps. The initial treatment with caustic soda is similar to that which takes place on mercerization—that is, the cellulose adsorbs sodium hydroxide and swells, the swelling being accompanied by an increase in the degree of dispersion. This renders the cellulose more reactive. Then the carbon disulfide is added and a metathetical reaction occurs. Cross and Bevan have shown that the best proportions of reagents are 2 molecules of sodium hydroxide and 1 of disulfide to each  $C_6H_{10}O_5$  aggregate. The usual reaction between carbon disulfide and an alcoholic alkali requires only 1 molecule of the alkali, so that it looks as if the second molecule of sodium hydroxide, apparently necessary for the reaction, is held to the cellulose by adsorption. The product is really, therefore, an alkali cellulose xanthate. Only one of the three hydroxyl groups of cellulose seems to be concerned in the reaction. After from 12 to 24 hours, Cross and Bevan have shown, the proportion of cellulose to xanthate radical corresponds to one xanthate radical to two  $C_6H_{10}O_5$  aggregates, and this compound passes continuously to one in which there are four  $C_6H_{10}O_5$  aggregates to each xanthate radical. This latter compound represents the material which spontaneously gels from a viscose solution. It is, however, soluble in aqueous alkalis.

The solution of viscose is probably to be explained as a colloidal dispersion of the alkali cellulose xanthate in water. This dispersion is not stable; it breaks up again on standing at normal temperatures. This behavior gives an excellent example of

hysteresis. The viscose first forms a continuous phase—or, in other words, gels—and then the gel shrinks symmetrically with exudation of solvent. The material possesses remarkable power to absorb water, as will be seen when it is pointed out that as little as 1 per cent viscose in solution will form a gel, and solutions containing 12 to 15 per cent no longer shrink spontaneously.

Viscose solution may be precipitated by alcohol or brine. If the precipitate is redissolved and again precipitated, it is found that the percentage of  $\text{Na}_2\text{O}$  and sulfur in the compound gradually diminishes as the process is repeated, no break being observed in the curve between the original xanthate and the cellulose hydrate, which is the limiting product.

Another way of coagulating viscose is by heat. When evaporated at a low temperature, a solution of viscose gives a water-soluble residue. If heated to 80 or 90°C., a viscose solution coagulates, and, if dried at this temperature, gives a residue which is not soluble in water. In either case, an analysis indicates that more water is adsorbed by such residues than by the original cellulose. This seems to indicate an increase in the degree of dispersion, as is further evidenced by the fact that the product dyes more readily, is more easily acetylated, and also adsorbs a larger amount of sodium hydroxide from solution than normal cellulose.

The chief practical significance of viscose lies in the fact that it is the basis of one of the most successful of the processes for manufacturing artificial silk. In this connection it has been discovered that the preliminary treatment of cellulose with sodium hydroxide solution is not merely a swelling, but that from the practical point of view it is advantageous that a certain amount of oxidation of the cellulose also take place. Patents have been taken out which cover the use of sodium peroxide,<sup>17</sup> and also the use of catalysts, such as iron or nickel hydroxide.<sup>18</sup>

After the viscose has been prepared according to the general method outlined above, it is carefully filtered and then forced under pressure through very fine orifices into a coagulating bath. Different solutions have been used for this purpose, such as dilute sulfuric acid and sodium bisulfite solution. The threads as they

<sup>17</sup> Eng. Pat. 13055 (1914) to Courtauld, Glover, and Wilson.

<sup>18</sup> Eng. Pat. 14675 (1914) to Courtauld and Wilson.



leave the coagulating bath are carefully washed, freed from sulfur and other impurities, and bleached if desired.

### CELLULOSE NITRATE

When cellulose is treated with concentrated nitric acid, a true nitric acid ester is formed. Since the cellulose remains solid during the treatment, one of the factors determining the degree of nitration is the surface exposed. Probably the most common way of modifying the amount of surface is to add concentrated sulfuric acid, which is adsorbed by the fiber and not only aids the reaction by increasing the degree of dispersion of the cellulose but also acts as a direct catalyst of the esterification. The highest nitrate known is the one containing three nitrate groups for each  $C_6H_{10}O_5$  aggregate. This is usually referred to as the hexanitrate. There seems to be an unbroken series of compounds with steadily but gradually decreasing amounts of combined nitric acid from this point down to hydrocellulose. The compounds with the highest nitrogen content are among our best explosives. Those with an intermediate amount form the basis of the nitrocellulose plastic industry, while those with the least nitrogen have no particular commercial significance.

The mechanism of the nitration reaction is not clear, but there is reason for believing that it takes place in steps so that there is always present a large number of nitrocelluloses of differing degrees of nitration. Technically speaking, conditions of time, temperature, and acid proportions are controlled to give chiefly the desired nitrate, but the product is by no means homogeneous. The reason for this is quickly seen when it is recalled that the nitric acid not only "nitrates" but also hydrolyzes, oxidizes, and saponifies, while there is also the hydrolyzing and saponifying action of the sulfuric acid to be considered.

The manufacture of celluloid from nitrocellulose affords a very interesting example of applied colloid chemistry. In the usual American process for making celluloid, the moist pyroxylin is intimately ground with about one-quarter of its weight of camphor. The water is then expelled by pressure and, after the resulting cake has been broken up, it is slowly sprayed with denatured alcohol and thoroughly stirred at the same time. Alcohol amounting to about 10 per cent of the weight of the



pyroxylin is ordinarily used. The resulting mixture is allowed to stand for some hours to allow for proper impregnation by the alcohol and is then worked on warm rolls until translucent, when it is pressed into slabs and sheeted or given some other form. It is finally seasoned in driers at 50°C. to remove any volatile solvent which may remain. From the colloid point of view, the finished product is a true colloidal gel. The mechanical properties of the finished celluloid are dependent to some extent upon the manipulation which it receives in the plastic state.

Sproxton<sup>19</sup> believes that, in the manufacture of solid celluloid from nitrocellulose, we have to do with the gradual transformation of a gel to a solid. In other words, except for the possible momentary formation of a sol at the surface of the fibrous nitrocellulose when the liquid solvent first comes into contact with it, there is no time during the process when we are dealing with a true sol. The change from gel to solid is due to a loss of solvent, involving a loss in both weight and volume. Dubosc,<sup>20</sup> on the other hand, though admittedly with no experimental evidence to support his theory, regards celluloid as a "camphorgel" of nitrocellulose, camphor being the dispersion medium. In any case, the fact that there is an evolution of heat when nitrocellulose and camphor are worked together<sup>21</sup> would seem to indicate considerable changes in surface energy.

The manufacture of celluloid is, in reality, a rather complex problem in colloid chemistry, inasmuch as there are a great many factors to be taken into consideration. In the first place, there is the purification of the cotton. This is usually done by boiling with alkalis under pressure and it has been found that the conditions of this treatment, such as the concentration of alkali, the time of boiling, and the pressure, all exert a marked effect on the properties of the cellulose, which carry through to the properties of the finished celluloid.<sup>22</sup>

Following the purification of the cotton comes the nitration and on the conditions under which this is carried out depend not

<sup>19</sup> *Chem. Age* (London), **3** (1920), 474.

<sup>20</sup> *Caoutchouc & gutta-percha*, **16** (1919), 9803.

<sup>21</sup> SPROXTON: "Third Report on Colloid Chemistry," 1920, p. 85.

<sup>22</sup> GIBSON and MCCALL: *J. Soc. Chem. Ind.*, **39** (1920), 172T; GIBSON, SPENCER, and MCCALL: *Trans. Chem. Soc.*, **117** (1920), 479; PUNTER, R. A.: *J. Soc. Chem. Ind.*, **39** (1920), 333T.

only the degree of nitration but also the amount of modification which the cellulose may undergo, due to hydrolysis and similar causes. The amount of camphor used is also obviously of importance. It has recently been shown<sup>23</sup> that, with a given nitrocellulose, the amount of camphor in relation to the proportion of alcohol has a marked effect on the viscosity of the resulting mixture. As camphor is added, the viscosity at first decreases and, with increasing amounts of camphor, finally reaches a minimum. As the proportion of camphor is increased after that, the viscosity rises. The water content of the alcohol is also of importance, since too much water prevents gelatinization of the nitrocellulose.

**Solutions of Nitrocellulose.**—Solutions of nitrocellulose are used to a considerable extent as lacquers, enamels, and as special varnishes known as "dopes," which serve to tauten and waterproof the wings of airplanes. They consist essentially of colloidal dispersions of nitrocellulose in suitable organic solvents, often with the addition of gums and sometimes pigments. Nitrocellulose is soluble in acetone, ethyl, butyl, and amyl acetates, mixtures of alcohol and ether, and certain other solvents. It is also often possible to add to a concentrated solution some non-solvent like benzene or denatured alcohol as a diluent without coagulating the nitrocellulose. A plasticizing agent, such as camphor or some camphor substitute, may also be added to impart desired properties to the finish when dry.

Owing, perhaps, to the fact that they are non-aqueous solutions, the colloid chemistry of nitrocellulose solutions has not been studied a great deal. As early as 1911, however, it was found that solutions of cellulose nitrate in acetone do not dialyze through pig's bladder or through parchment paper, and, furthermore, that they exert no osmotic pressure. Somewhat later, however,<sup>24</sup> it was shown that, if membranes of denitrated nitrocellulose were used, acetone solutions of nitrocellulose did exert osmotic pressure and there was even a partial dialysis. These apparently contradictory results have been reconciled by Ostwald,<sup>25</sup> who pointed out that methods which have been developed

<sup>23</sup> ATSUKI: *J. Coll. Eng. Tokyo Ind. Univ.*, **13** (1922), 1.

<sup>24</sup> DUCLAUX and WOLLMAN: *Compt. rend.*, **152**, 1580; *Bull. Soc. Chim.* (4), **27** (1920), 414.

<sup>25</sup> Report on the Physics and Chemistry of Colloids, British Dept. of Scientific & Industrial Research, 1920, p. 89.

for the characterization of aqueous colloid systems, as, for example, dialysis, are not necessarily applicable to non-aqueous systems. It must, for example, be established that any given membrane is neither too dense nor too permeable to permit of differentiation between molecularly and colloiddally dispersed substances.

When cellulose nitrate is dissolved in an organic solvent, a colloidal solution is obtained in which the cellulose compound is dispersed in the solvent in the form of a lyophile colloid. In common with all lyophile solutions, it is noticed that the viscosity of any given solution increases at a very much more rapid rate than the concentration of the solution. Furthermore, the viscosity of these solutions gradually decreases when they are subjected to mechanical treatment, such as shaking or pressing through capillary tubes.

This is sometimes explained as indicating a sort of structure, even in the liquid, and as being connected with liquid membranes which surround the colloidal particle. That it really also affects the substance which is in the dispersed phase is indicated by the fact that when a given sample of cellulose nitrate is dissolved, which necessarily involves a certain amount of mechanical treatment in the way of stirring, and is then recovered from the solution in some manner, either by evaporating the solvent or by precipitation in a non-solvent and drying, the recovered cellulose nitrate gives solutions of a lower viscosity than solutions of similar concentration made from the original nitrate.

Cellulose nitrate solutions also show rapid changes in viscosity with variations in temperature, and the viscosity of the solution is influenced by its thermal history. It is very interesting to note that, in making up lacquers or other solutions in which gums are included as well as a cellulose ester, it makes a decided difference in the finished solution whether the cellulose ester is added to the solvent first or whether the gum is added before the cellulose ester. Sometimes the effect is so marked that, if the gum is added to the solvent first, the cellulose ester will not dissolve in the resulting mixture, but, if the cellulose ester is added first, the gum can be readily dissolved afterward. In other words, the cellulose ester is not soluble in the colloidal dispersion of the gum in the solvent, although the gum may be dispersed in the



solution of cellulose ester. From this it would appear as if the cellulose ester and solvent formed the dispersion medium, and the gum the dispersed phase, and that it was not possible under the conditions cited to obtain a mixture in which the solvent, plus gum, was the dispersion medium with the cellulose ester as dispersed phase.

Of considerable interest from the theoretical standpoint, though perhaps of less practical value, is a recent study<sup>26</sup> of the behavior of nitrocellulose in contact with dry ether at low temperatures. It was found that at  $-20^{\circ}\text{C}$ . nitrocellulose begins to dissolve in absolute ether and on lowering the temperature to  $-98^{\circ}$  the viscosity approaches an asymptotic limit value. It was found by quantitative study that the laws of colloidal chemistry which apply to aqueous systems hold similarly for this non-aqueous system.

It is, of course, well known that different samples of nitrocellulose vary in their resistance to heat. Under such conditions it has been found that a sample of nitrocellulose which has been heated gives a solution with a lower viscosity than the same sample before heating, and, further, there seems to be a direct relation between the decrease in viscosity and the stability of the sample under observation.<sup>27</sup>

Another interesting colloidal property of cellulose nitrate is the fact that it can serve as an emulsifying agent<sup>28</sup> for dispersing water or glycerin in amyl acetate or other organic solvents for nitrocellulose. In this connection it is interesting to note that films of cellulose nitrate were observed around drops of water dispersed in an amyl acetate-benzene solution.

Cellulose nitrate is also of technical importance because of the fact that it was the basis of the first successful process for the manufacture of artificial silk. The same process with some modification is still in successful operation in this country as well as in Europe. The silk is known as "Chardonet" or "Lehner" silk, the former being the name of the original inventor of the process and the latter the name of the man who made important modifications. The process consists essentially in dissolving

<sup>26</sup> KUGELMASS: *Rec. trav. chim.*, **41** (1922), 751.

<sup>27</sup> DUCLAUX: *J. Soc. chim.*, **29** (1921), 374.

<sup>28</sup> HOLMES and CAMERON: *J. Am. Chem. Soc.*, **44** (1922), 66.



cellulose nitrate in a mixture of alcohol and ether and then forcing the carefully filtered solution into water or into air. In either case the filaments are wound on suitable bobbins, but before they can be used they must be treated with calcium or ammonium hydrosulfide to remove the nitro group. One of the particular characteristics of this process is the fact that filaments of smaller sizes can be made by this process than by any of the other methods in use in this country.

**Cellulose Acetate.**—An acetic acid ester of cellulose results when cellulose is treated with acetic anhydride in the presence of a catalyst, such as zinc chloride, sulfuric acid, methylamine sulfate, etc. There are two general methods of producing cellulose acetate, both of which have a number of variations. One results in a fibrous cellulose acetate, resembling in outward appearance the original cotton used as raw material; the other gives a granular product. Both have this in common—that the catalyst is adsorbed on the fiber and presumably facilitates the reaction not only because of its true catalytic effect, as exhibited in any esterification, but also because it causes a swelling and probably an increase in the degree of dispersion of the cellulose. Sometimes, in practice, time is allowed for this adsorption of catalyst and resulting swelling before the acetic anhydride is added. That the degree of dispersion of the cellulose is really modified is indicated by the fact that the longer the preliminary treatment the more rapid the reaction when the anhydride is added and the less viscous the solutions of the product.

In making the granular form of cellulose acetate, cellulose, usually in the form of cotton, is treated with a mixture of acetic acid, acetic anhydride, and a suitable catalyst. The acetic acid acts merely as a carrier and takes no part in the reaction. The catalyst, dissolved in acetic acid, is frequently mixed with the cellulose some time before the anhydride is added, although in other cases all are added together. Since cellulose acetate is soluble in acetic acid, the cellulose dissolves as the esterification proceeds. Samples are taken from time to time and, when the desired solubility has been attained, the reaction is stopped by adding an excess of water, which destroys any remaining anhydride and precipitates the cellulose acetate.

In the earlier processes the acetate thus formed was the triacetate, which corresponds to the hexanitrate. It later developed that, owing to their wider range of solubility, the acetates of most technical usefulness were those with a somewhat lower acetyl content than would correspond to a hexa-acetate on the  $C_{12}$  basis, but higher than would correspond to a tetra-acetate. These were at first prepared by adding small and carefully regulated amounts of water and sulfuric acid to the solution of cellulose acetate. As before, when the desired solubility was attained, the product was isolated by precipitation with water. While, outwardly, this secondary treatment is one of partial saponification, actually it is much more intimately connected with the colloid properties of the cellulose acetate, since an equivalent degree of saponification obtained by methods not involving the solution of the acetate does not give a product with the same wide range of solubilities.

In preparing cellulose acetate in fibrous form, it is given a preliminary treatment with sulfuric acid dissolved in glacial acetic acid, this step being similar to the one for preparing granular cellulose acetate. During this treatment the cellulose adsorbs sulfuric acid to such a degree that the amount adsorbed has to be taken into account in making up the bath for the following run. After removing the surplus preliminary bath in a centrifuge or press the cellulose is immersed in a mixture of acetic acid, acetic anhydride, and some non-solvent hydrocarbon. The sulfuric acid catalyst, being adsorbed directly on the fiber, is in a particularly favorable position to hasten the reaction. The proportion of non-solvent is so regulated that the cellulose acetate does not dissolve. When the product has reached the desired degree of solubility, the surplus liquid is removed and the residue is thoroughly washed with water. The product is cellulose triacetate, and, in order to render it soluble in acetone, it may be subjected to a partial saponification, as in the case of the granular form described above.

Cellulose acetate is used to a limited extent in the manufacture of non-inflammable plastics, airplane dopes, moving picture films, and artificial silk. Cellulose acetate silk is made by dissolving the cellulose acetate in a suitable organic solvent. The solvent used depends upon the solubility of the acetate which is

employed. In general, however, the solvents are either acetone or a mixture of tetrachlorethane and alcohol. In either case the solution is forced under pressure through very fine orifices into a liquid with which the solvent is miscible but which is in itself not a solvent for cellulose acetate. The thread is wound up on spools as it leaves the precipitating bath and, after suitable washing and drying, it is ready for use.

Cellulose acetate silk is distinguished from the other varieties of artificial silk by the fact that it is a true ester of cellulose in its finished form, while the other commercial varieties of artificial silk are forms of hydrated cellulose. Because of this distinctive chemical property, cellulose acetate silk behaves towards many dyestuffs in a manner different from other varieties of artificial silk and also different from wool and cotton. As a result, its use enables the dyer to obtain many interesting piece-dyed effects.

The colloid chemistry of cellulose acetate plastics is the same in its essential principles as that of celluloid, and, accordingly, need not be considered further at this point. It may be of interest, however, to consider briefly what probably happens when a solution of cellulose acetate evaporates, as, for example, in the drying of lacquer or airplane dope, or in the manufacture of continuous films such as are used for photographic purposes. In the simplest case the cellulose acetate is dispersed in the solvent. As this is spread out on a surface to dry, the solvent gradually evaporates, and, finally, at a certain concentration a gel is formed. The solvent continues to evaporate, until finally we reach a condition where the solvent becomes the dispersed phase and the cellulose acetate the dispersion medium. This may, perhaps, be the situation in films which have become brittle.

If, on the other hand, we were to start with a cellulose ester solution containing, in addition to the cellulose ester and solvent, some material analogous to camphor which, though solid, was still a solvent of the cellulose ester, then, on continued evaporation of the liquid solvent from the gel, the solid and non-volatile solvent would remain, and we would have a true gel with two continuous phases, which, with a suitable camphor substitute, would not be brittle.

In selecting such a solid solvent it is desirable to select a material which is miscible with the cellulose ester over a wide range of concentrations, for certain such materials are known which, although acting as camphor substitutes in certain proportions, still, if these concentrations are materially increased, tend to form a crystalline deposit which, of course, renders the combination unfit for practical purposes.

An interesting study of organosols and gels of cellulose acetate has been made by Mardles,<sup>29</sup> using the Tyndall cone and viscosity changes. He finds that the change from sol to gel is gradual and consists of three separate steps: first, "condensation," or the union of particles in a common film; second, "aggregation," or the approach of these larger particles closer together; and, third, "linkage." The usual effects of temperature change, concentration, previous history, and mechanical agitation were found to apply as well to dispersions of cellulose acetate in benzyl alcohol as to the more common dispersions of lyophile colloids in water.

#### CELLULOSE ETHERS

During the last 10 years, considerable experimentation has been carried out on still another group of cellulose compounds, the cellulose ethers, and a considerable number of patents have appeared covering methods for their preparation and use. In general, the methods used are the same as those employed for preparing aliphatic ethers, *viz.*, the action of alkyl halides upon the sodium alcoholate of cellulose or the action of diethyl sulfate on cellulose. Cellulose, however, does not respond so readily to these reactions as it does to esterification and it is, therefore, necessary to make the cellulose more reactive either by converting it into the alcoholate, which, of course, also involves an increase in the degree of dispersion, or else by dispersing it in a suitable solvent. According to Lilienfeld,<sup>30</sup> cellulose is dissolved in alkali, then precipitated by mineral acids, and, finally, redissolved in sodium hydroxide. This solution is then treated with diethyl sulfate to form the ethyl ether. Denham and Woodhouse<sup>31</sup>

<sup>29</sup> *Trans. Faraday Soc.*, preprint (1922).

<sup>30</sup> French patent 447974, Jan. 20, 1913.

<sup>31</sup> *J. Chem. Soc.*, **103** (1913), 1735; **119** (1921), 77.



do not dissolve the cellulose, but merely allow it to swell for several days in a sodium hydroxide solution. The alkaline cellulose is then treated with an excess of the alkyl sulfate. Bayer and Company have patented a process<sup>32</sup> in which the cellulose is given a preliminary treatment of swelling in concentrated sodium hydroxide solutions for a day or two. The excess alkali is removed, the product dried, and treated with a suitable alkyl halide under pressure for about 8 hours.

In all of these methods a mixture of the mono, di, and triethers is obtained, but under proper conditions it is possible to obtain a product consisting largely of the triether, indicating that all three of the hydroxyl groups of the cellulose have reacted. The resulting ethers are soluble in alcohol, chloroform, benzene, carbon tetrachloride, ethyl acetate, acetone, and other organic solvents. They are beginning to appear on the market in a limited way, particularly in the form of transparent films.

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<sup>32</sup> German patent 322586, Kl. 120, Jan. 26, 1912.

## CHAPTER XXVIII

### RUBBER

By

G. STAFFORD WHITBY

#### LATEX

The latex of *Hevea brasiliensis*, from which almost all the raw rubber used today is obtained, is a colloidal system of no little complexity, into the behavior of which a very considerable number of factors enter. The globules do not consist simply of a single chemical individual, *viz.*, the hydrocarbon, caoutchouc; the aqueous serum contains both a protective colloid (protein) and a variety of crystalloids; possibly other components, soluble neither in the globules nor the serum, are adsorbed on the globules; the coagulation phenomena are probably complicated by the intervention of an enzyme; and, finally, the behavior of the latex is influenced by the active bacterial growth which occurs in it under the conditions in which it is normally handled in the tropics. Further, the addition of preservative chemicals to latex very considerably modifies its behavior; and, as a considerable amount of preserved latex is now being imported for industrial purposes from the tropics, the behavior of such latex demands special consideration and study.

Latex is a white fluid of about the consistency of cow's milk cream and contains normally 30 to 40 per cent of rubber. The globules, which are in Brownian movement, range from about 0.5 to  $3\mu$  in diameter and, according to Bobilioff,<sup>1</sup> consist of four kinds, *viz.*: (1) very small, round globules, less than  $0.5\mu$  in diameter, (2) round globules, 1 to  $2\mu$  in diameter, (3) pear-shaped globules, 1.5 to  $2\mu$  wide, (4) tailed, pear-shaped globules, 1.5 to  $3\mu$  in diameter. F. E. Lloyd informs the writer that in the course of the examination of a large number of samples of latex pre-

<sup>1</sup> *Archief voor de Rubbercultuur*, 3 (1919), 374.

served with ammonia he has found pear-shaped globules to predominate. Cataphoresis experiments show the globules to be negatively charged.<sup>2</sup>

**Emulsoid or Suspensoid?**—Although latex is commonly described as an emulsoid, it is probably more correct to designate it a suspensoid. It was found<sup>3</sup> that the viscosity of latex (preserved) was proportional to the solid content up to a concentration of 10 per cent, but that beyond that it increased more rapidly than the concentration. And this has been urged as evidence that latex is an emulsoid. It must, however, be remembered that, even if latex is a suspensoid, it cannot for several reasons be expected to behave exactly like the classical suspensoids, such as gold or arsenious sulfide sols. The presence of protein, *i.e.*, of a hydrophylic emulsoid, to the not inconsiderable extent of more than 5 per cent of the weight of the caoutchouc, and the ready deformability of the material of which the suspended particles consist—these, and possibly other, unrecognized factors would naturally modify the behavior of the suspensoid.

It is further to be remarked that the globules are in all probability not, as was suggested earlier,<sup>4</sup> composed of a liquid, an oily precursor from which caoutchouc arises during coagulation, but consist of caoutchouc itself, that is, of a solid, albeit an elastic one.<sup>5</sup>

While our classificatory system for colloids is only at its present stage of refinement, the somewhat nice question as to whether latex is more properly denominated a suspensoid or an emulsoid can perhaps be left open. At all events, latex is a lyophobic colloid system: the material of the globules is practically without affinity for the aqueous medium. The viscosity of a system caoutchouc/aqueous medium, such as is represented

<sup>2</sup> HENRI: *Compt. rend.*, **144** (1907), 431; CLINGETT: *Rubber Recueil*, Amsterdam, **114** (1914), 377.

<sup>3</sup> BORROWMAN: "The Rubber Industry," London, 1911, p. 243.

<sup>4</sup> WEBER, C. O.: *Ber.*, **36** (1903), 3108.

<sup>5</sup> Good recent evidence for this is de Vries' demonstration (*Arch. Rubber-cultuur*, **3** (1919), 183) that the specific gravity of latex globules is the same as that of rubber in bulk.

It may be noticed, too, that the fact that the latex globules in many cases exhibit a non-spherical shape is perhaps some indication that the material of which they are composed is solid.

by latex, is very much less than that of a system caoutchouc/rubber "solvent" of the same concentration in caoutchouc. Van Rossem<sup>6</sup> states that the relative viscosity of a 5 per cent solution of masticated rubber in benzene is more than a hundred times as great as that of latex of the same concentration. In the one case the caoutchouc is dispersed in a liquid which swells or solvates it, and the system is an emulsoid one; in the other case, caoutchouc is dispersed in a liquid which does not swell it, and the system is probably a suspensoid one.

**The Emulsifying Agent.**—As the material of the globules is practically incapable of swelling in the aqueous medium in which it occurs in latex, an emulsifying agent or emulsifying agents must be present. In all probability the main agent responsible for maintaining the caoutchouc in dispersion is protein, playing the part of a protective colloid. About half the protein present in latex is retained by the rolled coagulum in the ordinary method of preparing rubber from latex.<sup>7</sup> At all events, the portion of the protein which is left in the latex serum after coagulation can act as an emulsifying agent, as is clearly indicated by the fact, shown both by determinations of interfacial tensions and by the preparation of actual emulsions of benzene in water, that the solid matter in the serum is a good emulsifier. Experiments show<sup>8</sup> that a phytosterol which occurs in rubber in small amount is a good emulsifying agent, but it is doubtful at the moment whether this substance plays any part in the dispersion of the globules in latex. The main crystalloid constituent of latex, quebrachitol, is practically devoid of emulsifying power. A careful search failed to reveal the presence of a saponin in latex.

Some experiments have of late been made on the preparation of artificial dispersions of rubber—artificial latex, taking dry rubber as the starting-out material. Such dispersions were first prepared by Pohle,<sup>9</sup> who worked with synthetic methyl caoutchouc. It was found impossible to disperse the dry caoutchouc directly; and Pohle's procedure was to atomize a solution

<sup>6</sup> *Chem. Weekblad*, **20** (1923), nos. 9 and 10; DELFT: "Rubber Latex and its Industrial Importance," 1923, p. 16.

<sup>7</sup> It is here assumed that substantially the whole of the nitrogen present represents protein.

<sup>8</sup> WHITBY and DOLID: Meeting Amer. Chem. Soc., Apr., 1923.

<sup>9</sup> *Kolloidchem. Beihefte*, **13** (1920), 1.



of the caoutchouc by means of carbon dioxide into a dilute soap solution. This author was not successful in obtaining a dispersion with a concentration at all approaching that of latex; the dispersions obtained were not milky in appearance; and in only one case was the dispersion stable enough for the performance of coagulation experiments. In this case alcohol and also acid caused a separation of the droplets. More satisfactory artificial dispersions of natural rubber with the aid of soaps have subsequently been obtained by several authors.<sup>10</sup> In all cases the rubber was "dissolved," in, say, benzene, prior to the preparation of the dispersion. Tuttle has shown that, after the dispersion of the dissolved rubber has been made, the benzene can be removed by stirring and heating in a closed system, without destroying the dispersion. As is pointed out later, the caoutchouc occurring in natural latex is already in a slightly swollen or "dissolved" condition, so that, even if the rubber "solvent" used in the preparation of artificial latex is not removed, its presence in the disperse phase does not necessarily invalidate analogies that may be drawn between the system and natural latex. The fact that, in the method of making emulsions just described, the rubber is dissolved in a liquid which is emulsifiable in water is an essential feature, for attempts made by the author to form a dispersion of rubber in water by using a solution of rubber in a water-miscible liquid (*viz.*, diethylamine) and introducing it into a solution of a soap or of gelatin were unsuccessful.

**Coagulation.**—In the industrial preparation of raw rubber, coagulation of the latex is almost invariably brought about by the addition of acetic acid, the proportion of the latter employed being about 0.5 per cent of the weight of rubber present. With fresh latex, coagulation is probably not a simple case of the coagulation of negatively charged suspensoid particles by means of cations, and not even a case of a direct effect of the acid on the protective colloid; it appears, rather, that the acid produces coagulation by hastening the action of an enzyme present in the latex.<sup>11</sup> The coagulating enzyme acts presumably on the

<sup>10</sup> TUTTLE: *India Rubber World* (1922–1923); PELIZZOLA: *Giorn. Chim. Ind. Appl.*, **5** (1923), 76; WHITBY and WINN: *J. Soc. Chem. Ind.*, **42** (1923), 336T.

<sup>11</sup> BARROWCLIFF: *J. Soc. Chem. Ind.*, **37** (1918), 489; WHITBY: *Kolloid-Z*, **12** (1913), 147; *Malayan Agr. Bull.*, **6** (1918), 374.

protective colloid. An analogous case would be the coagulation of milk by rennin, assisted by the addition of an amount of acid insufficient by itself to coagulate the milk. The evidence in favor of the view that an enzyme is concerned in the coagulation of latex is circumstantial only; the hypothetical enzyme has not been isolated, and some writers do not accept the view just outlined.<sup>12</sup>

As has recently been pointed out by de Vries,<sup>13</sup> and as the present writer had also observed, preserved latex differs from fresh latex in its behavior towards acids in a way that is in accord with the view that an enzyme is concerned in the coagulation of the latter but not in that of the former. No matter what proportion of acid is added to fresh latex, immediate clotting cannot be obtained: even under the most favorable conditions several minutes elapse before a clot forms, just as some time is required for the clotting of milk by rennin. On the other hand, latex which has been preserved by ammonia, and which is a month or more old, clots immediately if sufficient acid is added, the hypothetical enzyme having disappeared.

An oxidizing enzyme occurs in latex, but is in all probability without influence on the coagulation of the latter.

The globules in latex almost certainly consist not of caoutchouc only, but contain some of the substances which can later be found

<sup>12</sup> EATON: *Malayan Agr. Bull.*, **4** (1915), 426; VERNET, *Le Caoutchouc* **16** (1919), 9825.

Since the above was written, de Vries (*Rec. trav. chim. Pays-Bas*, **42** (1923), 701) has brought forward new evidence clearly indicating that an enzyme is concerned in the formation of a clot from latex. He finds, for example, that latex which has been treated in such a way (by dilution and sterilization) that the addition of acetic acid will produce only "creaming" may be caused to give a coherent clot on standing overnight by the introduction of as little as 1 part in 256,000 of fresh, unsterilized latex.

He finds, further, that, if a certain large amount of acid is added to the fresh latex before its introduction, the latex is not effective in producing a clot. This affords an explanation of the observation (WHITEY: *Kolloid-Z.*, **12** (1913), 147) that, on adding to fresh latex increasing quantities of hydrochloric acid in excess of the minimal amount required to produce coagulation, a point is reached when no coagulation occurs. This concentration of acid apparently kills the enzyme or inhibits its activity.

<sup>13</sup> *Archief Rubbercultuur*, **7** (1923), 168.

in an acetone extract of the coagulum obtained from the latex. In particular, they almost certainly contain the fatty acids of which the acetone extract has recently been shown largely to consist, for it has been shown that fatty acids can swell rubber.<sup>14</sup>

The chemical composition of the washed and dried coagulum obtained by the usual procedure from *Hevea* latex is, roughly, as follows: caoutchouc, 94.5 per cent; resin, 3.0 per cent; protein (*i.e.*,  $N \times 6.25$ ), 2.25 per cent; ash, 0.25 per cent. The amount of solids left in the serum is of the order of 10 per cent of the weight of the coagulum. About half the weight of serum solids consists of quebrachitol (the monomethylether of hexahydroxycyclohexane); the remainder consists of protein, inorganic matter, and unidentified substances.

**Adsorption by Latex Globules.**—The globules in latex show a remarkable capacity for retaining, in presumably an adsorbed condition, substances, present in the latex, which are insoluble in the material of the globules. The most striking example of this is perhaps to be seen in the invariable occurrence, observed by the writer, of quebrachitol in rubber samples. This substance is retained by the coagulum, despite the fact that it is, at tropical temperatures, soluble in approximately its own weight of water, and that the coagulum may be subjected to a considerable amount of mastication on a mill over the rolls of which water flows continuously.

During coagulation the globules readily take up water-soluble (non-fat-soluble and, therefore, presumably non-caoutchouc-soluble) dyes which may be added to latex; and such dyes are retained by the coagulum despite the fact that the wet coagulum may be masticated and rolled out into crêpe in a stream of water.<sup>15</sup> This behavior renders the preparation of colored raw rubber easy, although at present such rubber is not prepared commercially.

### SWELLING

In no respect is rubber more obviously or typically colloidal in its behavior than towards liquids which cause it to swell or "dissolve." When placed in certain organic liquids, rubber

<sup>14</sup> WHITBY: Meeting Amer. Chem. Soc., Apr., 1923.

<sup>15</sup> WHITBY: *Kolloid-Z.*, **12** (1913), 147; *Rubber Age* (London) **4** (1923), 134.

gradually imbibes the liquid in question and swells. In the case of raw rubber, the imbibition generally proceeds so far that, especially if stirring or other mechanical agitation is applied, the swollen rubber becomes dispersed through the liquid, and a "solution" results. In the case of vulcanized rubber the swelling proceeds to a smaller extent—an extent which diminishes with increase in the degree of vulcanization—and the rubber does not become dispersed. No hard and fast line can, however, be drawn between raw and vulcanized rubber with respect to the extent of swelling: all samples of raw rubber do not swell to such an extent as to be readily dispersible, nor is the swelling of all samples of vulcanized rubber limited to such an extent that dispersion does not follow.

Raw rubber in the form of crêpe is easily dispersible, whereas many samples of unmilled Fine Hard Para rubber, or of rubber prepared by the evaporation of latex, swell without dispersion occurring. It would appear that raw rubber, in the preparation of which no mechanical treatment has been used, swells without dispersing, whereas raw rubber, in the preparation of which there has been applied mechanical treatment (rolling in the case of sheet, more severe rolling accompanied by tearing in the case of crêpe), or, especially, milling of the dry rubber (involving both mechanical treatment and the application of heat) tends to become dispersed when it is swollen in a suitable liquid.

In the case of vulcanized rubber, a gradual fall in the degree of swelling accompanies a gradually increasing degree of vulcanization. Rubber vulcanized to the extent usual in technical practice swells only to a limited extent and cannot be dispersed, but rubber which has been only very slightly vulcanized swells to such an extent that a solution of it is obtainable, and rubber in which vulcanization has been carried very far, as in the case of ebonite, shows substantially no swelling at all. Stevens<sup>16</sup> found that, when the vulcanization of a mixture of 90 parts of rubber and 10 parts of sulfur was carried only to such an extent that the combined sulfur amounted to 0.3 per cent, the product could be readily dispersed in benzene.<sup>17</sup>

<sup>16</sup> *J. Soc. Chem. Ind.*, **38** (1919), 192T.

<sup>17</sup> Cf. VAN HEURN: "Mededeelingen van den Rijksvoorlichtingsdienst te Delft," 1916, p. 410.



**Swelling Agents.**—Rubber stands contrasted to most of the materials on the swelling of which observations have been made, in that, whereas the latter—gelatin, glue, starch, gum arabic, cellulose, silica, chitin, etc.—swell in water and not in organic liquids, rubber does not swell appreciably in water, but swells in certain organic liquids. The generally recognized swelling agents for rubber are hydrocarbons (aromatic and aliphatic), halogenated hydrocarbons, and carbon disulfide. Recent observations<sup>18</sup> show that, in addition to such long-known swelling agents, substances belonging to a number of other classes are capable of swelling rubber. A survey of the behavior of raw rubber to a large number of organic liquids indicates the existence of a broad relation between the ability of organic liquids to swell rubber, and their dielectric constants.<sup>19</sup> Thus, speaking broadly, substances in the following classes, which have generally high dielectric constants, produce little or no swelling, *viz.*, alcohols, aldehydes, ketones, esters, acid anhydrides, acid amides, nitriles, and nitrohydrocarbons, while, on the other hand, substances in the following classes, which have generally low dielectric constants, produce swelling, *viz.*, hydrocarbons (including terpenes), halogenated hydrocarbons, ethers, acids,<sup>20</sup> and amines.<sup>21</sup> It was a little surprising to find that substances so different chemically as amines, silicon tetrachloride, and fatty acids should have the common property of swelling rubber. A comparatively low dielectric constant is, however, common to these substances. Among amines it was found that, parallel with their generally higher dielectric constants, secondary amines produce more swelling than corresponding primary amines.

An apparent exception to the relation just noted is presented by the mustard oils, which have comparatively high dielectric constants but are good swelling agents for rubber.

The materials other than rubber, on the swelling of which quantitative data are available, *viz.*, proteins, such as gelatin, and carbohydrates, such as starch, swell in water—a liquid of

<sup>18</sup> WHITBY: Meeting Amer. Chem. Soc., Apr., 1923.

<sup>19</sup> *Cf.* p. 670.

<sup>20</sup> An exception is to be made of the first two members of the fatty acid series. These have high dielectric constants.

<sup>21</sup> A swelling agent, the dielectric constant of which has not been recorded, but which is probably low, is azobenzene.

high dielectric constant, which favors the occurrence of electrostatic phenomena; further, in the case of the proteins the swelling substance is amphoteric, and the swelling phenomena exhibited are much subject to ionic influences. Rubber, which is composed substantially of the hydrocarbon caoutchouc, swells in liquids which, like itself, have low dielectric constants; and it would seem to offer a case in which the phenomenon of swelling may be examined without the complicating circumstances present in the case, for example, of gelatin.

A case which bears some analogy to the case of rubber is that of the silver salts of the fatty acids.<sup>22</sup> The silver soaps do not swell in water, but have been found by the writer to swell, dissolve, and often, on cooling, give gels when they are heated with liquids belonging to the same classes as those which swell rubber, *i.e.*, hydrocarbons, halogenated hydrocarbons, carbon disulfide, ethers, fatty acids, mustard oils—liquids which, with the exception of the last mentioned, possess, in general, low dielectric constants.

**Data on the Swelling of Raw Rubber.**—By choosing a form of raw rubber, *viz.*, unmilled Fine Hard Para, which swells only to a limited extent and does not become dispersed when the liquid is shaken gently, Posnjak<sup>23</sup> and also Spence and Kratz<sup>24</sup> were able to make some quantitative measurements of the swelling of unvulcanized rubber in a number of liquids. Posnjak used an "oedometer," in which the swelling of the rubber, contained in a porous cell immersed in the swelling liquid, could be ascertained under a definite pressure by means of the movement, in a capillary tube, of the mercury column which rested on the rubber. He found that the higher the pressure applied to the rubber, the less did the latter swell; that, under a definite pressure, equilibrium was reached; and that this equilibrium was the same at the same pressure, whether the pressure was reached by raising or by lowering. The following table shows the volumes, calculated as percentages of the volume of the unswollen rubber,<sup>25</sup> of 11 liquids imbibed under a pressure of 1,120 g.

<sup>22</sup> Cf. WHITBY: *Science*, **53** (1921), 580.

<sup>23</sup> *Kolloidchem. Beihefte*, **3** (1912), 417.

<sup>24</sup> *Kolloid-Z.*, **15** (1914), 217.

<sup>25</sup> Calculated from Posnjak's data by KIRCHHOF: *Kolloid-Z.*, **6** (1914), 1.

TABLE I

Carbon tetrachloride.....	679	Benzene.....	500
Chloroform.....	625	Thiophene.....	500
Tetrachlorethane (sym.).....	610	Cumene.....	470
Toluene.....	525	Ether.....	325
Acetylene dichloride.....	510	Ethylene chloride.....	211
Cymene.....	510		

Spence and Kratz determined the swelling of disks of raw rubber, 2.5 to 3 mm. thick, both by measuring and by weighing them. In general, the swelling had substantially reached its limit after 72 hours' immersion. The following table shows the percentage volumes of several liquids imbibed after 10 days' immersion.

TABLE II

Carbon tetrachloride.....	1,205	Xylene.....	889
Chloroform.....	1,130	Ether.....	482
Carbon disulfide.....	1,007	Methyl alcohol.....	13
Toluene.....	952	Ethyl alcohol.....	—
Benzene.....	905	Acetone.....	—

It will be observed that benzene and its two homologs show very similar swelling ability, and that, as in the measurements made by Posnjak under pressure, the chlorinated paraffins produce more swelling than aromatic hydrocarbons.

**Velocity of Swelling.**—Posnjak concluded that there was a constant relation between the swelling pressure,  $P$ , to which the rubber was subjected, and the amount of liquid which it imbibed:

$$P = P_1 c^k$$

where  $c$  is the concentration of rubber in the swollen mass, and  $P_1$  and  $k$  are constants,  $k$  being always about 3, and  $P_1$  varying from liquid to liquid. The velocity of swelling in any given case ran like a reaction of the first order, being expressible with very fair accuracy by the general Newton's time, which was first applied to swelling processes by Wo. Pauli.<sup>26</sup>

$$x = \frac{1}{z} \ln \frac{\omega_{\infty}}{\omega_{\infty} - \omega}$$

where  $\omega_{\infty}$  and  $\omega$  represent the cubic centimeters of liquid taken up at the limit of swelling and at time  $z$  respectively, and  $x$  is a constant.

<sup>26</sup> OSTWALD, WO.: "Grundriss der Kolloid Chemie," 1909, p. 369.

Measurements of the rate of swelling of vulcanized rubber made by Flusin<sup>27</sup> can, Posnjak states, be similarly expressed.

Tompkins<sup>28</sup> had earlier found that the rate of swelling of vulcanized rubber in a pure liquid, *e.g.*, carbon disulfide, agreed for a considerable distance with the equation  $\omega = k \log z$ , and remarked that the equation did not seem to be related to Fick's law of diffusion. Also Lundal<sup>29</sup> and Kirchhof<sup>30</sup> have pointed out that the velocity of swelling is great at first and then falls off, and further have shown that, in general, rise in temperature increases both the rate of swelling and the amount taken up when swelling has reached its limit. Rise of temperature has relatively less effect in increasing the velocity of swelling and the swelling maximum in the case of more highly vulcanized than in the case of less highly vulcanized rubber samples. The magnitude of the effect of temperature on the rate of swelling may be indicated by the following example.<sup>31</sup> After 4 hours' immersion in a paraffin oil at 100°, a pure-gum vulcanized rubber has absorbed 3.485 g. per gram, whereas at 16° about 450 hours' immersion was required for absorption to proceed to the same extent.

The swelling of raw rubber in benzene is accompanied by a contraction, which, however, is much smaller than the contraction observed when gelatin or starch swells in water.<sup>32</sup>

**Effect of Swelling on Elastic Properties.**—When vulcanized rubber<sup>23</sup> was swollen in paraffin oil, it was found by Lundal<sup>34</sup> first to diminish in density and then to increase. A change in compressibility paralleled the change in density, the compressibility reaching a maximum approximately at the point when the density reached a minimum.

It is of interest to inquire whether the act of swelling rubber so alters it that, on allowing the swelling liquid to evaporate, the

<sup>27</sup> *Compt. rend.*, **126** (1898), 1479; *Ann. Chim. Phys.*, **13** (1908), 480.

<sup>28</sup> *Diss. London*, 1896; Discussion Faraday Soc. and Phys. Soc., London (1921), 162.

<sup>29</sup> *Ann. Phys.*, **66** (1898), 741.

<sup>30</sup> *Loc. cit.*

<sup>31</sup> LUNDAL: *Loc. cit.*

<sup>32</sup> POSNJAK: *Loc. cit.*

<sup>33</sup> The rubber was black and had a density at 17.4° of 0.90166.

<sup>34</sup> *Loc. cit.*



mechanical properties of the rubber will have undergone important changes. Van Heurn<sup>35</sup> concluded that the swelling of sheet rubber in benzene not only rendered the rubber more readily extensible under a given load, but also increased the ultimate tensile strength, as the following data show:

	PERCENTAGE ELONGATION AT RUPTURE	TENSILE STRENGTH (KG./CM. <sup>2</sup> )
(a) Untreated sheet.....	527	10.4
(b) Sheet swollen in benzene and then dried.....	864	12.1

The question may, however, be raised as to whether, in view of the great difficulty of removing the last traces of a swelling liquid from rubber (*vide infra*), this result is not influenced by the retention of benzene by the rubber.

Lundal<sup>36</sup> compared the mechanical behavior of a pure-gum vulcanized rubber, which had imbibed 68.9 per cent of paraffin in one case and 133.5 per cent of paraffin oil in another case, with the behavior of the original rubber, and found that, although the elastic modulus of each of the swollen samples was lower than that of the original rubber (the samples agreeing in this respect with van Heurn's raw rubber sample mentioned above), their elastic behavior was not essentially different: the Joule effect (*i.e.*, the contraction of stretched rubber when heated) and associated phenomena were displayed.

**Data on the Swelling of Vulcanized Rubber.**—The swelling of vulcanized rubber is not essentially different from that of raw rubber, although the swelling is smaller in extent and is never followed by dispersion, except in samples so slightly vulcanized that, from an industrial viewpoint, they can hardly be considered as being vulcanized at all. The order in which swelling agents fall in regard to vulcanized rubber is practically the same as that in which they fall in regard to raw rubber, as shown in Tables I and II. For example, chlorinated paraffin hydrocarbons produce more swelling than aromatic hydrocarbons. The following table shows results obtained by Tompkins<sup>37</sup> with "black rubber tubing (S. G. 1.06)."

<sup>35</sup> *Mededeelingen Rijksvoorlichtingsdienst te Delft* (1916), 442, 357; *Communications Netherlands Government Rubber Inst.* (1917), 98.

<sup>36</sup> *Loc. cit.*

<sup>37</sup> *Loc. cit.*

TABLE III.—PERCENTAGE VOLUMES OF LIQUIDS IMBIBED<sup>38</sup>

Chloroform.....	737	Ether.....	309
Carbon disulfide.....	652	Ethyl acetate.....	71
Benzene.....	587	Acetone.....	27

The following table shows results obtained by Flusin<sup>39</sup> for a sample of rubber of sp. gr. 0.997 at 17°, ash content 2 per cent, total sulfur content 12.54 per cent, combined sulfur content 1.28 per cent. The liquids are arranged in the order of the amounts of swelling produced after 24 hours (column c). The data in columns *a* and *b* will be referred to later. Liquids which produce considerable swelling were classed by Flusin as "active;" those which produce practically no swelling, as "inactive."

TABLE IV

Active liquids				Inactive liquids	
Liquid	Sp. gr. <i>a</i>	Percentage volume absorbed at 16°		Liquid	Percentage volume absorbed at 16°, after 24 hr.
		After 1 min. <i>b</i>	After 24 hr. <i>c</i>		
Chloroform.....	1.52	32.6	964	Ethyl acetate.....	33.0
Carbon disulfide.....	1.26	64.9	811	Acetone.....	15.0
Toluene.....	0.88	24.2	740	Acetic acid.....	12.0
Xylene.....	....	15.4	635	Amyl alcohol.....	8.5
Benzene.....	0.88	17.1	586	Ethyl alcohol.....	2.5
Turpentine.....	0.86	4.3	552	Methyl alcohol.....	2.0
Benzyl chloride.....	1.11	6.8	439	96 % Ethyl alcohol..	1.1
Petrolie ether.....	....	12.6	438	Water.....	0.5
Kerosene.....	....	2.7	367		
Ether.....	0.72	18.7	343		
Nitrobenzene.....	1.20	2.0	136		

Kirchhof<sup>40</sup> examined a series of samples vulcanized, from a 100: 12.5 rubber-sulfur mixture, to different extents. The results with carbon tetrachloride may be quoted as typical.

<sup>38</sup> Data recalculated from Tompkin's.

<sup>39</sup> *Loc. cit.*

<sup>40</sup> *Kolloidchem. Beihefte*, 6 (1914), 1.

TABLE V

	Coefficient of vulcanization				
	1.2	2.0	3.6	4.4	6.4
Percentage volume of carbon tetrachloride absorbed:					
After 1 hour.....	709	586	512	404	340
After 6 hours.....	2,410	1,430	982	774	512
After 24 hours.....	2,900	1,610	1,040	787	540

It will be observed that, the higher the degree of vulcanization, the smaller is the amount of swelling and the more rapidly does the velocity of swelling fall off. For the series of samples in question, the relation between the swelling in a number of liquids which were examined and the degree of vulcanization could be expressed very well by the equation:

$$\omega K \epsilon = k$$

where  $\omega$  is the swelling,  $K$  the coefficient of vulcanization,  $\epsilon$  an exponent depending on the nature of the swelling medium, and  $k$  a constant. The coefficients of vulcanization calculated from this formula differed from the figures determined analytically by only about 0.1 to 0.2.

**Swelling in Vapors.**—The swelling of rubber in the vapor of swelling liquids, when compared with the swelling in such liquids themselves, presents some interesting features. Pohle<sup>41</sup> found that the weight of material absorbed by raw rubber when it was placed in a 1:1 mixture of benzene and paraffin oil at room temperature (this represented a tension of 53 cm. of mercury as against one of 60 cm. for pure benzene) was uninfluenced by mastication or other preliminary treatment to which the rubber might be subjected. Samples as follows: (a) untreated sheet, (b) the soluble part of a, (c) a reprecipitated, (d) sheet masticated, (e) d reprecipitated, (f) the soluble part of unmilled Fine Hard Para, (g) f reprecipitated—all showed an absorption of from 66 to 70 per cent of their weight.

<sup>41</sup> *Loc. cit.*

Kirchhof<sup>42</sup> found that the amount of material taken up by his samples of vulcanized rubber (*supra*) from the vapor of boiling liquids was independent of the degree of vulcanization and was the same as that taken up by the unvulcanized substance, although this amount varied with different liquids. The amount of absorption was much less than that following immersion in the liquids themselves, as a comparison of the following table with Table V will show.

TABLE VI.—PERCENTAGES ABSORBED AFTER 1 HOUR IN VAPOR

	Coefficient of vulcanization					
	0.0	1.2	2.0	3.5	4.4	6.4
Carbon tetrachloride.....	99	97.5	99	98	99	105
Benzene.....	98	89.5	87	86	86	85
Carbon disulfide.....	..	64.0	65	63	64	67

Tompkins<sup>43</sup> has given reasons for believing that, when absorbed by rubber, such vapors become liquefied.

Thermal effects are observable when raw rubber is immersed in various vapors. Experiments with thermoelectric junctions covered with films of rubber showed that heating occurs when rubber is immersed in the vapor of ether, benzene, pyridine, toluene, chloroform, water, and ammonia.<sup>44</sup>

**Rubber as a Semi-permeable Membrane.**—The behavior of rubber as a semi-permeable membrane appears to be dependent upon its ability to swell in some liquids and its failure to swell in others. Raoult<sup>45</sup> observed that, if ether and alcohol are separated by a rubber membrane, ether passes into the alcohol; and at his suggestion Flusin<sup>46</sup> studied the osmosis of a considerable range of liquids across a membrane of vulcanized rubber.<sup>47</sup> When water was on one side of the diaphragm and methyl alcohol,

<sup>42</sup> *Loc. cit.*

<sup>43</sup> *Loc. cit.*

<sup>44</sup> HOUGHTON: *Proc. Phys. Soc.*, **35** (1922), 39.

<sup>45</sup> *Compt. rend.*, **121** (1895), 187; *Z. physik. Chem.*, **17** (1895), 737.

<sup>46</sup> *Loc. cit.*

<sup>47</sup> For a description of the rubber used, see p. 664.



ethyl alcohol, or acetic acid on the other, no osmotic movement took place; but, when alcohol was on one side and any of the "active" liquids mentioned in Table IV on the other, the liquid in question passed more or less rapidly into the alcohol. Flusin measured the speed of osmosis in the case of each of these active liquids, and found the speeds to be in the order in which the liquids fell in regard to the volume of liquid absorbed by the rubber, not when swelling was allowed to proceed to its limit (*vide* column *c*, Table IV), but when the amount of swelling was determined after only a short immersion; that is to say, the order in which the liquids fell if arranged according to the figures shown in column *b*, Table IV. The absorption during the early stages of immersion does not bear a constant relation to the limiting absorption, but, it will be observed (*vide* column *a*, Table IV), is influenced by the specific gravity of the liquid; ether, for example, being at first absorbed to a greater extent than benzene, although ultimately absorbed to a smaller extent.

When the liquids were examined in pairs, not against alcohol but against each other, it was found that in all cases the liquid showing a higher initial absorption passed through the membrane more quickly than the liquid showing a lower. Kahlenberg<sup>48</sup> verified this, but found that there was a minor current in the reverse direction. He concluded that the conditions for the passage of a liquid from one side of a rubber membrane into a liquid on the other were (1) that the rubber must be capable of imbibing the liquid, and also (2) that the moving liquid must be miscible with the other liquid. He found, further, that rubber acted as a semi-permeable membrane to solutions in pyridine of substances, such as silver nitrate, lithium chloride, and sugar, which are insoluble in rubber; but that it was permeable to copper oleate dissolved in pyridine or benzene, copper oleate being soluble in rubber.

**Swelling and Osmotic Pressure.**—A very suggestive treatment, from the viewpoint of the osmotic pressure of the liquids in question, has been made by Tompkins<sup>49</sup> of the effect on swollen rubber of the addition of small quantities of various liquids to a liquid in which a sample of swollen rubber is immersed. He assumes that the swelling of colloids is due to osmotic pressure; that in the

<sup>48</sup> *J. Phys. Chem.*, **10** (1906), 159.

<sup>49</sup> *Loc. cit.*

swollen colloid we have a material sensitive to such pressure; and that the change in volume which an addition to the swelling liquid produces represents the osmotic pressure of such addition.

"Black rubber tubing (Sp.Gr. 1.06)" was swollen in carbon disulfide, and various liquids were then added to the latter. In all cases the influence of the addition could be expressed fairly accurately by

$$p - ap^2 = kv$$

where  $p$  is the mean number of gram-molecules of the added liquid inside and outside the rubber,  $v$  the change in volume produced by the addition, and  $a$  and  $k$  constants. With very small percentages of an added liquid, the term  $ap^2$  would disappear, and hence there would be in all cases an increase in volume at first, and such increase would be proportional to the amount of dissolved substance; *i.e.*, on the assumption that the change in volume really represents the osmotic pressure of the dissolved substance, the expansion would at first be proportional to the number of molecules of the substance present, the latter exercising a pressure equivalent to that of a perfect gas. But, as the quantity of the added liquid increased, there would be, as shown in van der Waals' equation for a gas, a negative pressure, represented by  $ap^2$ , due to the mutual attraction of the molecules of the liquid. And, in fact, Tompkins found that when increasing quantities of acetone were added to the carbon disulfide in which a piece of swollen rubber was immersed, the volume at first increased, and then diminished, as is shown by the results in the following table.

TABLE VII

Gram-molecules acetone per cubic centimeter (mean of amounts inside and outside the rubber).....	0	0.00054	0.00099	0.00188	0.00290
Volume of expanded rubber.....	100	102.58	103.76	104.14	100.57
Gram-molecules acetone per cubic centimeter (mean of amounts inside and outside the rubber).....	0	0.00411	0.00504	0.00555	0.00669
Volume of expanded rubber.....		86.93	71.52	58.76	32.77

Chloroform, benzene, ether, ethyl acetate—liquids which, unlike acetone, swell rubber—were found in all proportions to increase the swelling when added to the carbon disulfide, and to behave as perfect gases over a much greater range of concentration than did acetone, the values calculated from the equation agreeing with the observed values over a greater distance. The magnitude of the effect which may thus be produced by mixing swelling agents may be indicated by an example: Taking the maximal swelling in carbon disulfide alone as 100, that in benzene alone was 91.41, while that in the optimum mixture of carbon disulfide and benzene was 107.

**Nature of Swelling.**—While it cannot be said that the real nature of the forces involved in swelling is understood any more than is the nature of those involved in ordinary solution, it is nevertheless possible to draw some sort of picture of the swelling process in the case of rubber.

Freundlich and Posnjak<sup>50</sup> consider that, aside from the idea of swelling representing a chemical phenomenon, three possibilities have to be reckoned with; namely: (1) that swelling is a purely capillary process, a liquid being taken up in the spaces between the units (say, globules) of the gel, without any change occurring in the size of the units; (2) that swelling is a pure solution process, the units dissolving the liquid and so changing in size, density, etc.; (3) that swelling is both a capillary and a solution process. These authors favored the capillary conception. It has, however, been pointed out by Kirchhof<sup>51</sup> that capillary action, if involved at all in the swelling of rubber, can normally play only a small part, since the weight of different liquids taken up is not, on Posnjak's own data, in the ratio of the densities, and since some liquids ("inactive" liquids) behave so differently from others ("active" liquids).

Tompkins<sup>52</sup> considered that, in the swelling of rubber in a liquid, the liquid diffuses into the rubber until its osmotic pressure is balanced by the volume elasticity of the colloid.<sup>53</sup> Kirchhof

<sup>50</sup> Cf. POSNJAK: *Kolloidchem. Beihefte*, **3** (1912), 417.

<sup>51</sup> *Kolloidchem. Beihefte*, **6** (1914), 1.

<sup>52</sup> *Loc. cit.*

<sup>53</sup> An explanation of the important Joule effect in rubber (*cf.* p. 663) from a similar point of view has been suggested by Tompkins. If it is

found, in experiments with the series of vulcanizates mentioned on page 665, that, just as there was a relation between swelling and the coefficient of vulcanization, so was there a clear relation between the mechanical strength of the rubber and its degree of swelling—as the extensibility fell, so did the amount of swelling. In this connection it is of interest to note that, if the heating of a rubber-sulfur mixture is continued after all the sulfur has entered into combination, a reversion occurs in regard to the swellability just as it does in regard to the tenacity; that is to say, the amount of swelling begins to increase just as does the extensibility.<sup>54</sup>

Tompkins concluded, further, that, since the rate of swelling *i.e.*, the velocity of diffusion of liquid into the rubber, in the case of the five liquids, carbon disulfide, chloroform, ethyl iodide, benzene, and ether, was approximately inversely proportional to the molecular weight, the rubber acted, as it were, like a sieve through which larger molecules enter more slowly than smaller ones. This holds, however, only for liquids, such as those just mentioned, which swell rubber largely, *i.e.*, which dissolve freely in it or have a high degree of affinity for it.

**Swelling and Dielectric Constant.**—The affinity of liquids or—what is, perhaps, essentially the same thing—the solubility of liquids in rubber, is probably connected with the dielectric constants of the liquids in question. Wo. Ostwald,<sup>55</sup> from a survey of the results of Flusin and of Posnjak for the swelling of rubber in a limited number of liquids (*vide supra*), suggested that the swelling power of liquids ( $\omega$ ) is inversely related to the dielectric constant  $D$  by the expression  $\sqrt[n]{\omega \cdot D} = k$ . The average value of  $n$  obtained from Flusin's data for 14 liquids was 2.16; and

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assumed, he says, that there is in rubber some diffusing substance, such as a portion of the rubber more fluid than the rest, the osmotic pressure of which in all directions is increased by heat, then such increase will assist the volume elasticity of those parts of the stretched rubber which are compressed, *i.e.*, the material along the shorter axis, and will oppose that of those parts which are expanded, *i.e.*, the material along the longer axis, thus producing a greater displacement in the first case than in the second, that is, leading to expansion along the shorter and contraction along the longer axis.

<sup>54</sup> PORRITT, B. D.: private communication.

<sup>55</sup> *Kolloid-Z.*, **19** (1921), 100.



from Posnjak's data for 4 liquids, 2.8. As mentioned earlier, a survey of a much larger range of organic liquids carried out by the present writer is in agreement with the conclusion that, at all events speaking broadly, liquids with low dielectric constants will swell rubber, while liquids with high dielectric constants fail to do so.

The full significance of the dielectric constant in this connection is not clear. It is to be noted, however, that substances with high dielectric constants are usually substances the molecules of which exhibit polarity and, therefore, substances in which the degree of mutual attraction between the molecules is high—so high that the molecules have no affinity for caoutchouc molecules. On the other hand, substances with low dielectric constants, being, in general, non-polar and having a comparatively low degree of mutual attraction between their molecules, readily associate themselves with caoutchouc, which also has a low dielectric constant.

It would seem probable that the forces involved in swelling are essentially similar to those involved in ordinary solution. Wo. Ostwald, while rejecting as too thoroughgoing the analogy between swelling and solution which is represented by the swelling theory of Katz, in which "uncomplicated swelling" and "solution" are identified, nevertheless points out that the relation between swelling and dielectric constant ( $\sqrt[n]{\omega \cdot D} = k$ ), to which he was led, is essentially the same as the relation between solubility and dielectric constant determined by Walden  $\left( \frac{D}{\sqrt[n]{\mu}} = k \right)$ .

In order to appreciate the similarity of these relations, it is necessary to note, however, that the analogue of swellability is not solubility ( $\mu$ ) in the ordinary sense (*i.e.*, mols per liter), but the reciprocal of this (liters per mol); that is to say, the volume of liquid required to bring 1 gram-molecule of a solid to complete liquefaction,  $\frac{1}{\mu}$ , is the real analogue of the volume of liquid which a given quantity of a swelling body will take up. Using this reciprocal solubility in Walden's equation, the latter becomes identical with Ostwald's. The exact value of  $n$  is uncertain in both cases; Walden gives it as 3 in his equation, Ostwald as between 2 and 3 in his.

## RUBBER SOLUTIONS

The question as to what occurs when swelling passes over into "solution" is of importance to a discussion of the nature of the "colloidal solutions" derivable from a lyophillic colloid such as rubber. Even when the swelling of unvulcanized rubber proceeds to such an extent that the rubber "goes into solution," it is probable that we cannot speak of *unlimited* swelling. The rigidity of the swollen product derived from raw rubber may be so low that the product becomes dispersed; nevertheless, it would seem, the amount of liquid associated with the rubber is still limited. A "solution" of raw rubber can be pictured as consisting essentially of the swollen gel in residual, unbound solvent.<sup>56</sup> This conception will account for the rapid rise in the viscosity of rubber solutions with increase in concentration, and also, since the amount of swelling is different in different liquids and shows some parallelism with the viscosity in different solvents, for the differences in viscosity of rubber solutions of the same concentration in different liquids.

**Solvent Bound by the Rubber.**—For a number of solutions, the viscosity of which he had measured, Kirchhof<sup>57</sup> calculated the percentage volume of the system occupied by the rubber + the swelling agent bound to it, by using the equation developed for emulsoids by Hatschek:<sup>58</sup>

$$A = \left( \frac{\eta}{\eta - 1} \right)^3$$

where  $A = \frac{\text{Total volume of system}}{\text{Volume of the disperse phase}}$ , and  $\eta$  = the viscosity.

The data for two solvents which belong to classes giving markedly different viscosities and also markedly different degrees

<sup>56</sup> Bary (*Compt. rend.*, **152** (1911), 1386) supposes that, when rubber "dissolves," swelling continues until the limit of elasticity of the rubber is reached, when the swollen mass disintegrates, after which breaking up into smaller and smaller aggregates continues until the joint effect of the surface tension of the reduced particles and their elasticity is in equilibrium with the attraction between the rubber and the solvent. It would not, however, seem to be necessary to assume such a disintegration of the gel.

<sup>57</sup> *Kolloid-Z.*, **15** (1914), 30.

<sup>58</sup> *Kolloid-Z.*, **7** (1910), 301; **8** (1911), 34; **11** (1912), 284; **12** (1913), 238; *Trans. Faraday Soc.*, **9** (1913), 80.

of swelling, *viz.*, an aromatic hydrocarbon and a halogenated paraffin, are shown in the following table.

TABLE VIII

	Concentration										
	0.5 %			1 %			2 %			3 %	
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>
Benzene.....	2.4	16.5	0.6	4.7	51.5	2.0	23.5	91	18	97.3	(102)
Pentachlorethane	3.0	29.8	0.7	8.7	72.0	3.6	46.0	97	33	213.5	(103)

(a) Relative viscosity.

(b) Percentage of total volume occupied by the disperse phase.

(c) Concentration of the solution calculated as Quantity of rubber taken/Total volume - Volume of disperse phase.

It will be seen (columns *c*) that if the concentration of the solutions is calculated by taking as the volume of the dispersion medium, not the total volume of the liquid applied, but only that portion which is not bound to the rubber, then the rapid rise of viscosity with solutions containing increasing amounts of rubber is rendered understandable and a linear relation between concentration and viscosity can be described.

The applicability of Hatschek's equation to a series of 14 solutions of rubber in benzene, ranging from 0.1 to 1.0 per cent in strength, was examined by van Rossem;<sup>59</sup> and it was found that the equation ceased to hold beyond a concentration of 0.45 per cent. Van Rossem's solutions were higher in viscosity and in the percentage volume occupied by the disperse phase than Kirchhof's. Thus, whereas the 0.5 per cent solution of the latter had a relative viscosity of 2.1 and a volume percentage of 14.6 occupied by the disperse phase, the corresponding figures for the 0.5 per cent solution of the former were 10.8 and 74.6. Van Rossem concluded that in the case of his solutions the amount of benzene which the rubber would take up to form the disperse phase was (giving the very approximate value of 1 to the density of rubber) 160 times the volume of the rubber, and, hence, that in the more concentrated solutions, which Hatschek's equation did not fit with strictness, there was insufficient benzene to satisfy the rubber.

<sup>59</sup> *Communications Netherlands Government Rubber Inst.* (1917), 73.

**Effect of Temperature, etc. on Viscosity.**—The viscosity of rubber solutions is very susceptible to various treatments to which the solutions or the raw rubber from which they are to be prepared may be subjected. Preliminary mastication of the raw rubber on a mill,<sup>60</sup> the action of light,<sup>61</sup> of ultra-violet light,<sup>62</sup> and of heat<sup>63</sup> on the solution—these and some other modes of physical treatment reduce the viscosity, often very greatly. As typical of such physical treatments, it is to be noted that the effect of heat on swelling and its effect on the viscosity of solutions are opposite; swelling being increased, while viscosity is reduced. The observation that heat increases swelling was, however, made with vulcanized rubber. And, if the picture of rubber solutions outlined above is accepted, it must be supposed that, when raw rubber is heated after it has been dispersed, *i.e.*, after it has swollen to its limit and the gel thus formed has been dispersed in excess of the liquid, the effect of heat is to make the rubber unable to hold all the liquid previously associated with it, *i.e.*, to reduce the degree of solvation. A similar syneresis of the gel phase would explain the fall in viscosity which rubber solutions often show on keeping.

**Viscosity and Osmotic Pressure.**—Some osmotic measurements made by Caspari<sup>64</sup> have a bearing on the question of the nature of the change which occurs when a rubber solution is heated. This author showed that the condition of a rubber solution which is connoted by its viscosity is connected with the osmotic pressure which it is capable of exercising. The osmotic rise produced by solutions of deresinated rubber in benzene was determined by an osmometer in which the semi-permeable membrane consisted of cold-vulcanized rubber. Similar determinations were made after solutions had been deviscified to some extent, and again

<sup>60</sup> Cf., *e.g.*, PORRITT: "Physics and Chemistry of Colloids," Faraday Soc. (London) 1921, p. 81.

<sup>61</sup> Vide, *e.g.*, FOL: *Mededeel. Rijksvoorlichtingsdienst te Delft* (1912), 22; *India-Rubber J.*, **43** (1913), 378; GORTER: *Meded. over Rubber, II*, Buitenzorg (1912); KIRCHHOF: *Kolloid-Z.*, **15** (1914), 30; VAN HEURN: *Mededeel. Rijksvoorlichtingsdienst te Delft* (1916), 357; PORRITT: *Loc. cit.*

<sup>62</sup> BERNSTEIN, HAMER: *Phys. Rev.*, **18** (1921), 331.

<sup>63</sup> Vide, *e.g.*, GAUNT: *J. Soc. Chem. Ind.*, **33** (1914), 446; CASPARI: *Trans. Chem. Soc.*, **115** (1914), 2139.

<sup>64</sup> *Trans. Chem. Soc.*, **105** (1914), 2139.



after solutions had been deviscified to an extreme degree (by boiling for 80 hours). The results, given in the following table, show (1) that, like the viscosity, the osmotic rise shown by rubber solutions increases far more rapidly than the concentration, (2) that the reduction in viscosity which heating produces is accompanied by a fall in osmotic pressure.

TABLE IX

Original solutions			Partly deviscified solutions			Highly deviscified solutions		
Concen- tration	Rise, in atms.	Viscosity, time of efflux, seconds	Concen- tration	Rise, in atms.	Viscosity, time of efflux, seconds	Concen- tration	Rise, in atms.	Viscosity, time of efflux, seconds
5.26	0.0592	.....	4.45	0.0235	771	9.95	0.0487	287
3.59	0.0307	.....	3.37	0.0158	402	6.89	0.0182	150
2.92	0.0214	.....	2.70	0.0116	285	4.11	0.0141	68
2.10	0.0117	3,196	2.17	0.0088	213	2.06	0.0060	35
1.48	0.0066	989	1.04	0.0036	86			
1.01	0.0036	374						

The dependence of the osmotic rise on the physical condition of solution was shown particularly conclusively by setting up osmometers with solutions, on either side of the septum, of the same material and concentration and differing only in viscosity. A more viscous solution always showed an osmotic rise against a less viscous one. Caspari points out that the dependence of the osmotic rise of caoutchouc solutions against the solvent on the physical condition of the solutions is most reasonably considered as deriving from a two-phase constitution on the part of such solutions; a gel phase and a sol phase being present, and deviscification connoting a shift of the equilibrium in favor of the sol phase. The observed osmotic rises may, then, be accounted for in either of two ways:

Either, firstly, the gel-phase is osmotically inoperative, and the rise depends solely on the concentration of the sol-phase. If this were so, it would follow that as the total concentration rises the sol-phase becomes more concentrated than the gel-phase, and that, as the viscosity of a given solution decreases, the sol-phase becomes more dilute. Or, secondly, so much of the gel-phase as is in contact with the diaphragm

(corresponding with the ratio of gel-volume to sol-volume in the liquid) exerts simultaneously a pressure of the same character as that which causes caoutchouc, gelatin, etc., to swell when immersed in solvents, the observed rise being then a composite one. One would then expect the pressure developed inside a semi-permeable diaphragm to reach as many atmospheres as the solution approached 100 per cent; and, indeed, the pressures capable of being exerted by swelling colloids are well known to be of no mean magnitude. Which alternative is the more probable it is not easy to decide in the present state of knowledge.

**Vulcanizing Quality and the Viscosity of Solutions.**—The feeling that the colloidal characteristics of rubber which are exhibited in the high viscosity of its solutions are, fundamentally, the same as those responsible for the valuable elastic properties exhibited after vulcanization has led to a widespread apprehension that the degree of viscosity of solutions of samples of rubber is related to the vulcanizing quality of the samples, and this had led to a good deal of attention being given to viscosity measurements as a possible means of evaluating raw rubber samples. In the absence, however, of any real understanding of the vulcanization process, of the intimate structure of vulcanized or of raw rubber, and of the relation of the viscosity of rubber solutions to the intimate structure of raw rubber, there is little or no solid ground upon which to base an apprehension such as that just mentioned. When, further, it is recalled that the viscosity of the solutions obtainable from a given sample of raw rubber can be greatly altered by physical treatment of the rubber, *e.g.*, by milling, without the occurrence of any substantial change in the vulcanizing properties of the rubber, it is hardly surprising to find that the degree of correlation between the viscosity of solutions of raw rubber samples and the elastic properties of vulcanizates obtainable from the samples is not very high.<sup>65</sup>

It is also to be noted that the viscosity of rubber solutions is very noticeably affected by small quantities of certain non-caoutchouc substances which may accompany the caoutchouc in natural rubber. This was remarked by de Vries, who has made extensive determinations of the viscosity of rubber samples.

<sup>65</sup> Cf., especially, DE VRIES: *Archief Rubbercultuur*, 2 (1918), 456; "Estate Rubber," Batavia, 1920, pp. 582 *et seq.*

Kruyt and Eggink<sup>66</sup> have measured the effect—which they believe to be an electroviscous one—of small quantities of the substances mentioned in Fig. 1 on the viscosity of 0.33 per cent solutions of rubber in benzene. All the substances examined, with the exception of ammonia, reduced the viscosity. The fall produced by small quantities of sulfur dioxide and of hydrochloric acid is particularly striking; 0.0365 g. of hydrochloric acid per liter of benzene reduced the viscosity by 15 per cent. Experi-

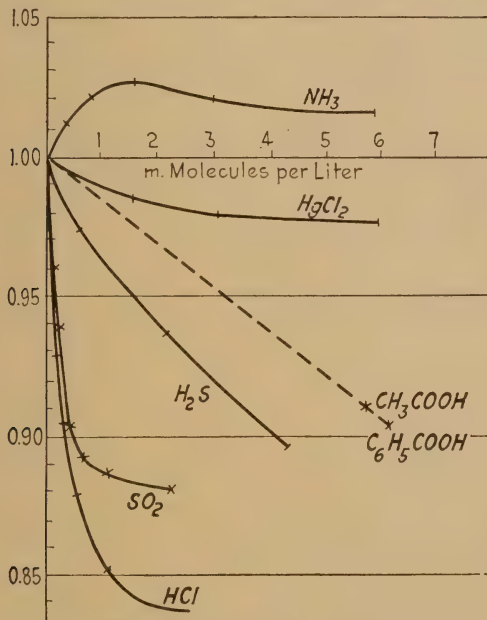


FIG. 1.—Electro-viscous effect in rubber solutions.

ments in the writer's laboratory show that small amounts both of organic acids and organic bases reduce the viscosity of sols of rubber in anhydrous benzene, the effectiveness of the different substances in either of these classes being apparently related to their dissociation constants as determined in aqueous solution.

Now, it has recently been shown that the resin which forms approximately 3 per cent of most samples of *Hevea* rubber consists largely of free acids, and, further, that samples of rubber

<sup>66</sup> *Proc. Roy. Acad., Rotterdam*, **26** (1923), 43.

vary very noticeably in the amount of resin acid which they contain.<sup>67</sup> When this is considered in the light of Kruyt and Eggink's results, it is clear that the resin content of rubber samples is a factor in determining the viscosity of their solutions. The presence of acid in the rubber resin will also explain the fact that, when rubber is fractionally dissolved, the first fraction has a lower viscosity than a later fraction, since the first fraction will have the highest resin content. The lower viscosity was, in fact, attributed to a higher resin content by Stevens<sup>68</sup> who made the original observation, although it was not at that time known that the resin contains a large proportion of acid.

**Influence of Residual Solvent on Solubility.**—The readiness with which raw rubber swells and goes into solution is markedly influenced by small amounts of swelling agents which it may initially contain. Stephens, working in the author's laboratory, has made a number of observations which illustrate this. For example, the readiness with which rubber, precipitated from solutions in benzene by the addition of alcohol or acetone, can be brought into solution again may be greatly influenced by the thoroughness with which traces of residual benzene are removed from it. Thus, two samples of precipitated rubber were heated at 110° for 8 hours, one sample in a sealed tube in nitrogen, and the other in a high vacuum. The former sample could be readily redissolved in benzene; the latter failed to disperse in that liquid.

A considerable proportion of the resin present in raw rubber undoubtedly acts as a swelling agent, for it consists of acids of types which swell rubber. Stephens found that, on evaporating a solution of masticated rubber to dryness, heating the residue at 100° in vacuo for 8 hours, and then allowing it to stand for 2 days, the rubber was quite as readily soluble as ordinary crêpe rubber, whereas, on evaporating a solution of rubber from which the resin had been exhaustively extracted, and giving the residue a similar treatment, a product was obtained which was almost insoluble.

It is probable that the so-called "b" (insoluble) form of caoutchouc of Harries<sup>69</sup> is simply rubber from which the resin has

<sup>67</sup> WHITBY and WINN: *Loc. cit.*

<sup>68</sup> *India Rubber J.*, **46** (1913), 345.

<sup>69</sup> *Ann.*, **383** (1911), 191.



been eliminated by extraction and precipitation, and the adhering solvent then more or less thoroughly removed. The "c" (oily) form of Harries, which is easily soluble in, *e.g.*, ether, probably simply represents the condition in which caoutchouc comes down, with a comparatively large amount of solvent obstinately associated with it, when it is precipitated from a solution which has been deviscified by heat or has stood for a long period.

**Relation of Protein Content to Swelling.**—It has been supposed by some writers that an important factor in the behavior of raw rubber towards swelling agents is the mode of distribution of the protein which is generally considered to constitute about 2.5 per cent of its weight. Spence<sup>70</sup> concluded, from the microscopic examination of sections of raw rubber, that protein films act as semi-permeable membranes, which allow the swelling liquid to pass in but do not allow the swollen rubber to pass out, so that dispersion of the rubber occurs only when swelling has proceeded to such an extent as to break the films or when the films have been previously broken by prior mechanical treatment of the rubber. This view is accepted by Kirchhof,<sup>71</sup> Stevens,<sup>72</sup> and others. Caspari,<sup>73</sup> however, adopted a sceptical attitude towards it; and, more recently, Pohle<sup>74</sup> has rejected it. Pohle points out that if a rubber solution is allowed to stand, so that a considerable proportion of the protein settles out, the protein-poorer rubber obtained on evaporation of the supernatant liquid does not show any greater ease of solution than the original rubber; and, further, that samples of synthetic caoutchouc, entirely lacking in protein, behave towards swelling agents essentially like natural rubber.

Observations made by Stephens in the author's laboratory also indicate that protein does not play an essential part in the swelling of rubber. For example, it was found that a sample of rubber, from which, by a fortunate circumstance, it had been possible to separate the whole of the protein, behaved like ordinary

<sup>70</sup> *J. Inst. Comml. Res. in Tropics*, Liverpool (1907), 47.

<sup>71</sup> *Kolloidchem. Beihefte*, 6 (1914), 1.

<sup>72</sup> Fourth British Association Report on Colloid Chemistry, London, 1922, p. 357.

<sup>73</sup> *J. Soc. Chem. Ind.*, 32 (1913), 1041.

<sup>74</sup> *Loc. cit.*

samples towards solvents; when, for example, the solvent was removed from the precipitated rubber by heating in vacuo at  $100^{\circ}$ , the product swelled in solvents without going into solution.

### VULCANIZATION

Although vulcanization is, from a technical viewpoint, by far the most important operation through which rubber is put, its nature presents what is still an unsolved problem, despite the fact that it has during the last 20 years been the subject of many investigations. It is impossible within the limits of the present chapter to embark upon an account or discussion of those investigations.

One conclusion that may be considered as now being almost universally accepted is that chemical reaction occurs when rubber is heated with sulfur, the end product of the reaction having the composition  $(C_5H_8S)_n$ ; and that the relation between the caoutchouc and the sulfur is not, as Wo. Ostwald<sup>75</sup> had suggested, merely one of adsorption. But it is, also, almost universally agreed that vulcanization involves something more than mere chemical reaction between caoutchouc and sulfur or other vulcanizing agent. An attractive hypothesis, due to Ostromislenski,<sup>76</sup> suggests that in vulcanization  $(C_5H_8S)_n$ , produced by reaction between sulfur and a comparatively small fraction of the caoutchouc, is adsorbed by or absorbs the chemically unchanged larger fraction of the caoutchouc. Experiments<sup>77</sup> in which rubber was heated with already-prepared  $(C_5H_8S)_n$  were, however, unfavorable to this theory, no vulcanization being obtained.

So far as our present knowledge goes, it may perhaps be said that the most reasonable tentative hypothesis as to the nature of vulcanized rubber is to regard such rubber as a dispersion of the sulfur reaction product  $(C_5H_8S)_n$  in caoutchouc.<sup>78</sup> A knowledge

<sup>75</sup> *Kolloid-Z.*, **6** (1910), 136.

<sup>76</sup> *J. Russ. Phys.-Chem. Soc.*, **47** (1915), 1453.

<sup>77</sup> WHITBY and JANE: Meeting Roy. Soc., Canada, 1923.

<sup>78</sup> Cf. Twiss' remark: "It may be hazarded that the wonderful effect of vulcanization itself is actually due to the production of a compound of sulfur and part of the rubber in an exceedingly finely dispersed condition throughout the remainder of the rubber mass." (*India Rubber J.* **65** (1923), 656.)

of the exact character of the relation between the rigid phase and the gel phase must probably await successful investigation of chemically simpler elastic gels. At all events, it may be remarked, the significant structure of vulcanized rubber is probably amicroscopic. The elastic properties may be surmised to derive from the nature of the caoutchouc phase and from the large interface developed between the phases. Soaps, the presence of which has been found to lead to increased tensile strength in vulcanized rubber,<sup>79</sup> would, on this hypothesis, be considered as producing their effect by increasing the degree of dispersion of the rigid phase.

The fact that vulcanized rubber still possesses, although in a reduced degree, the power to swell in certain liquids, which is possessed by unvulcanized rubber, may perhaps be considered as indicating that it consists in part of substantially unchanged caoutchouc; for, if the whole of the caoutchouc became chemically changed on vulcanization, it is improbable that it would retain the fundamental, colloidal property of swelling.

**Aging of Vulcanized Rubber.**—The nature of the changes, colloidal and chemical, which take place in vulcanized rubber during aging, and which are of great importance from a technical viewpoint, is not yet understood; and an elucidation of it will probably have to wait upon some measure of understanding of the real nature of vulcanization.<sup>80</sup> The changes in question flow from the vulcanization process, as raw rubber undergoes, on aging, comparatively little change with respect to the tensile properties of vulcanizates obtainable from it, especially if kept in a moist condition.<sup>81</sup>

**Vulcanization in Solution.**—The action of vulcanizing agents on rubber in solutions of sufficient concentration is to give a gel;<sup>82</sup>

<sup>79</sup> WHITBY and SIMMONS: Meeting Am. Chem. Soc., Apr., 1923.

<sup>80</sup> For data on aging, see GEER and EVANS: *India Rubber J.* **61** (1921), 1163; DE VRIES: *Archief Rubbercultuur*, **2** (1918), 792; STEVENS: *J. Soc. Chem. Ind.*, **39** (1920), 251T; PELIZZOLA: *Giorn. Chim. Ind. Appl.* **4** (1922), 458; MARZETTI: *Ibid.*, **5** (1923), 122.

<sup>81</sup> EATON and BISHOP: *J. Soc. Chem. Ind.*, **42** (1923), 389T; DE VRIES: "Estate Rubber," Batavia, 1920, pp. 348 *et seq.* Moisture also exercises a favorable action on the aging of vulcanized rubber (STEVENS: *Loc. cit.*).

<sup>82</sup> Particularly suggestive observations have been made by STEVENS: *J. Soc. Chem. Ind.*, **40** (1921), 186T. Cf. also STERN: *Z. Elektrochem.*,

that is to say, if we regard a rubber solution as a diluted rubber gel (*cf.* page 672), we find that, as with dry rubber, vulcanization leads to the development of greater mechanical strength. The gels obtained may undergo syneresis on keeping,<sup>83</sup> a phenomenon which may be analogous to fall in viscosity which rubber solutions show on keeping.

**Compounded Rubber.**—For most technical purposes, rubber is mixed on hot mills, prior to vulcanization, with powders such as zinc oxide, carbon black, or whiting. The readiness with which dispersions of such powders in the viscous medium in question are made may be increased by the introduction of small quantities of “softeners.”<sup>84</sup> Such softeners probably act in part by swelling or “diluting” the rubber and in part by affecting the interfacial relations between the rubber and the particles. The resin naturally present in rubber not improbably plays to some extent the part of a softener; for it is largely soluble in rubber, and has been found by the writer to be capable, thanks to its acid content, of assisting the wetting of a pigment, such as zinc oxide, by a vehicle, such as turpentine.

The means by which particulate substances when dispersed in rubber influence the tensile properties of the vulcanized product are now being actively studied.<sup>85</sup> The main factors governing the influence of a given substance are apparently: (1) assuming good dispersion, the fineness of the particles, *i.e.*, the extent of the rubber powder interface, and (2) the thoroughness of the wetting of the powder by the rubber, *i.e.*, the degree of cohesive force between them.

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15 (1909), 660; HINRICHSSEN and KINDSCHER: *Kolloid-Z.*, **11** (1912), 191; *Ber.*, **46** (1913), 1291. PORRITT: *Loc. cit.*; LE BLANC and KRÖGER: *Z. Elektrochem.*, **27** (1921), 335; BOIRY: *Compt.-rend.*, **175** (1922), 102.

<sup>83</sup> LE BLANC and KRÖGER: *Loc. cit.*

<sup>84</sup> *Cf.* AULTMAN and NORTH: *Ind. Eng. Chem.*, **15** (1923), 262.

<sup>85</sup> *Vide*, particularly, WIEGAND: *Can. Chem. J.*, **4** (1920), 160; *J. Ind. Eng. Chem.*, **13** (1921), 118; *cf.* also NORTH: *India Rubber World*, **63** (1920), 98. GRIEDER: *J. Ind. Eng. Chem.*, **14** (1922), 385; TWISS: *India Rubber J.*, **65** (1923), 607, 651, 693; GREEN: *Chem. Met. Eng.*, **28** (1923), 53.



## CHAPTER XXIX

### THE SIGNIFICANCE OF COLLOIDS IN THE DIETARY

By

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As the properties of heterogeneous systems are studied, chemists and physiologists are more and more appreciating the importance and significance of the colloidal nature of the components of protoplasm. It is owing to the peculiar properties of the boundary surfaces that protoplasm accomplishes its functions. What we call "organized" matter, in the sense in which we use this term in relation to living tissues, is capable of effecting the chemical changes associated with metabolism, by virtue of the distinct phases in which the components exist in the most intimate relation to each other. It seems necessary to conclude that the synthetic transformations and the separation of the products of metabolic activity in the living body are the inevitable result of the peculiar "organization" of the colloidal substances of which it is made.

With the exception of the inorganic compounds which are so essential in protoplasm, and with the exception, possibly, of the vitamins, by far the greater part of the material which we ingest as foodstuffs is in the form of colloids. The moiety of crystallizable organic substances in our foods represent, on the one hand, in the main, products which result from the action of digestive enzymes upon proteins, carbohydrates, and fats, and, on the other hand, metabolic end products.

In the early history of chemistry as applied to animal and plant life the assumption was generally made that the complexity of molecular structure of food substances was retained in great measure during digestion and absorption, and that this complexity, and also the peculiarities of the finer details, *e.g.*, of the protein molecules, were much the same in the animal tissues as in

the food proteins. In other words, the power of synthesis was regarded as the essential prerogative of the plant. Researches upon digestion and metabolism have all tended to emphasize the fact that the colloidal components of our foodstuffs lose their characteristic properties during digestion, through being cleaved into relatively simple substances, such as amino acids, glucose, fatty acids, etc.

### METABOLIC COLLOID PROCESSES IN THE BODY

The colloids of the tissues of the body represent products of synthesis from the simple cleavage products of the colloids degraded through digestion in the alimentary tract. The present-day knowledge of proteins offers abundant evidence that the colloids of the tissues, of this class at any rate, possess marked specificity in finer structure. It is known also that the structural peculiarities of proteins in no instance involve differences in the constituent amino acids of which they are built up, for the same optical forms of these building units are derived from different proteins upon hydrolysis.

On first thought, therefore, since during digestion the colloidal character of the food substances is lost, it might be deemed a matter of little or no importance whether our foods should contain colloids, or whether they should supply in the form of simple fragments (digestion products) all the chemical complexes necessary for the building of the body tissues. We shall see upon further analysis of the problem of nutrition that the colloidal characters of our principal foodstuffs have very important rôles to play.

Under natural conditions it is inevitable that the habit should have been established in all animals of securing their food principally in the form of colloidal matter. Animals eat either animal or plant tissues, which are largely composed of complex proteins, polysaccharides, and lipins. The necessity of transforming certain kinds of colloids into others of different internal architecture makes it imperative that these bodies shall lose their identity during the preliminary step in the series of events leading to assimilation of nutrients. This made necessary the development in all the higher animals of a digestive system.

An important function of the digestive tract, aside from the hydrolysis of the complex molecules of proteins, carbohydrates, etc., to a point where they have lost their individuality (in so far as this is essential in preparing the fragments of their giant molecules for functioning as construction units for the reconstitution of the more complex bodies of protoplasm of the several differentiated types found in the animal tissues) is the provision of nutriment for the body at a favorable rate. The importance of this will be better appreciated when we consider the dilution of the nutrient medium in which both plant and animal cells flourish best.

Single-celled organisms, which live in water and derive their nutrients from substances in solution in the medium in which they live, all obtain their food in great dilution. Those which contain chlorophyll and are capable of photosynthesis may thrive in water containing only one part of carbon dioxide in six millions of water. These cells require one part of nitrogen to twenty of carbon by weight for the synthesis of protoplasmic components, and can be nourished with respect to nitrogen in a medium which contains but one-half to two parts of nitrite nitrogen per million of water. Other nutrients may be furnished in like dilutions without interfering with the optimal growth of the organisms. Organisms which possess silicious skeletons derive this element from the dissolved silicon compounds in water of great dilution with respect to this element.

A remarkable illustration of the importance of high dilutions in nutrient solutions is afforded by the experiments of Moore<sup>1</sup> on the utilization of formaldehyde by green plants. This substance is a protoplasmic poison in concentration over 0.001 per cent. The demonstration was carried out by depriving algae of any source of carbon dioxide, and by introducing into the closed jars, containing the organisms and their nutrient medium, vessels containing solutions of formaldehyde sufficiently dilute so that they gave off the vapor of formaldehyde very slowly. This was dissolved by the nutrient solution in which the algae were kept, and at very great dilution. He found that they were able to synthesize carbohydrates from the formaldehyde when it was provided in so dilute a state as not to poison the cells.

These illustrations are so commonly employed as to be familiar to many, yet few appear to have reflected upon this phase of the rôle of colloids in animal nutrition. In the colloidal form the foodstuffs are not immediately available for absorption and are made available only slowly by digestion, and are thus prevented from entering the body fluids in concentrations sufficiently great to be harmful.

The injurious effects of a sugar content of the blood sufficiently high to cause glycosuria is well known. Whenever hyperglycemia exists, the rate of passage of glucose through the kidneys rapidly rises above the very slow rate of leakage characteristic of health, and this glycosuria is exceedingly damaging to the kidneys and must be guarded against by a restriction of the carbohydrates in the diet.

Again, the body is so constituted as to safeguard itself very effectively against an increase in the amino acid content of the blood. There appears to be no threshold value below which the amino acids are absolutely held back from passing through the kidneys, but the leakage is small so long as the concentration of these is kept sufficiently low in the blood. The animal body is provided, therefore, with a twofold mechanism for restricting the rate at which amino acids enter the blood.

The first of these is dependent upon the slow rate of digestion of proteins. A normal man may eat 16 to 18 g. of nitrogen in the form of protein during the course of a day, and, ordinarily, in three instalments. Each of these may require five or more hours for digestion and absorption. There will, of course, be a slow rate of amino acid production in the alimentary tract at the beginning and end of the digestive period, and a maximum rate at some time between these. Folin<sup>2</sup> has shown that the liver serves as a pool in the blood stream, into which the amino-acid-laden portal blood is poured and from which the amino acids escape but slowly into the systemic circulation. In this manner the systemic blood receives its digestion products of proteins at a much slower rate than would be the case if the blood from the several branches of the mesenteric vein were thrown directly into the general circulation. It is only under such favorable conditions that the tissues of the muscles and glandular organs are able to abstract from the blood the amino acids essential for



their growth or repair. Folin and Berglund have pointed out that the shrinkage of the liver in cirrhosis or atrophy, with its consequent diminution in blood content, eliminates this special function of the organ and results in abnormally high tides of amino acids in the systemic blood during absorption. Under these conditions the tissues cannot take up amino acids sufficiently fast, and, the kidneys being easily permeable to these, amino acids appear in abnormal amounts in the urine. It is on this basis that the tests for liver function are founded.

The property which enables the tissues, generally, to form glycogen from glucose, which they abstract from the blood, serves a twofold purpose. Through the deposition of glycogen there is provided a store of potential energy for the performance of work or for the maintenance of the normal temperature of the body. An equally important result of glycogen formation is the maintenance at a very low concentration, approximately 1 part in 1,000, of glucose in the blood.

There is a mechanism of comparable efficiency in the body for the provision, in the fluids which provide the cells with nutriment, of fats and other lipins at extreme dilution. The studies of Bloor on fat assimilation show how lipemia is prevented, even at the height of fat absorption, by the property of the erythrocytes which enables them to take up neutral fats from the blood, where they circulate for a short time in a finely emulsified form when brought in through the lymph duct, and to convert these into phospholipins, and into cholesterol esters. The fats are removed rapidly, so that within a short time after fat absorption has ceased the amounts of lipins in the plasma are so small that the latter is optically clear to the unaided eye. In the case of fats, as well as of proteins and carbohydrates, therefore, the body is prepared to withdraw, from the immediate environment of the cells, a plethora of nutrient complexes. This plan of nature for furnishing the living tissues of the higher animals with a nutrient solution of great dilution indicates that the animal cell, like the plant cell, is injured by the accumulation of nutrient principles in the medium surrounding it, as well as by the accumulation of the end products of nitrogen or carbon metabolism.

It is especially interesting to note that in the animal cell there is a very effective agency in its power to deaminize amino acids

and convert the resulting ammonia into urea, a substance of very low toxicity. Notwithstanding the fact that endogenous or tissue metabolism, with attendant destruction of protoplasm, must go on even when no materials are at hand for the support of repair, the body deals in a very prodigal way with its amino acid supply. Urea formation follows close upon the assimilation of amino acids by the tissues and the supply is soon exhausted, so that, within a few hours after protein digestion in the alimentary tract has ceased, the only source of the cleavage products of protein for the maintenance of those structures (heart, glandular organs, and nerve tissues), the uninterrupted functioning of which is imperative, is through self-digestion of muscle proteins and the transport of the resulting amino acids to the blood.

From the foregoing it will be seen that, notwithstanding the high degree of specilization reached by the higher animals, the cells which constitute the tissues have not had to adapt themselves to radical changes in environment, so far as concentration of their foodstuffs is concerned. Instead of such adaptation on the part of the tissues, there was evolution of the alimentary tract. In the higher animals whose food supply is likely to be precarious, the evolution of a stomach enables them to ingest a relatively large amount of food whenever it is available. They are then independent of food for an interval. The fact that the food is provided in forms not ready for assimilation, but requiring a thorough resolution through hydrolysis before absorption, aids the organism in presenting nutriment to its protoplasm in a manner strikingly similar to the primitive one in which the single-celled organism obtained its food in solution and in relatively simple forms. The colloidal structure of proteins and carbohydrates, and the insolubility of fats in aqueous systems, are fundamental to the success of this plan of nutrition for the more complex animal forms.

It is important for the welfare of the body tissues generally that the normal nutrient complexes, amino acids and glucose, shall not be allowed to accumulate in the blood in abnormal amounts. The kidneys are damaged by the passage through them of the digestion products of foods, as well as by the continued excretion of excessive amounts of metabolic end products of protein. Thus the aim of the physician in managing the diabetic

patient is so to regulate his diet that his urine shall remain sugar-free. This is done not only because the sugar lost does the patient no good, but because the excretion of sugar does positive harm. Polvogt, Simmonds, and the writer<sup>3</sup> have recently shown that the kidneys of rats are severely damaged by restricting them to diets containing excessive amounts of protein. The diets were so planned that the components other than protein were provided in relationships closely approximating the optimum. Newburgh<sup>4</sup> and also Park and Mendel<sup>5</sup> have observed the production of nephritis in animals which were fed excessive amounts of protein.

Another very significant result of our custom of taking our foodstuffs in the main in colloidal form relates to palatability. A mixture of amino acids is extremely unpalatable and it would be impossible for us to take a sufficient amount of each of the 18 or 20 indispensable digestion products of proteins in the form in which they are regularly absorbed from the intestine. Glutamic acid acts as an emetic when taken in the pure form, and the mixture of amino acids derived either from the acid hydrolysis or the enzymic digestion of protein is nauseating to the taste and, when presented to the lining membranes of the digestive tract in the concentration which would correspond to the amount of protein daily consumed by an average man taking the average amount of liquid, would be distinctly irritating.

When we take our amino acids in the form of proteins, we take them in a concatenated complex, chemically united, so that the individuality of each is lost, and its properties are masked. During digestion the protein molecule which, we have reason to believe, has a molecular weight of 12,000 to 15,000 and consists of about 100 amino acid molecules linked together in the dehydrated form, which is known as the peptide linkage, is resolved into its constituent amino acids through hydrolysis. This hydrolysis takes place sufficiently slowly so that the absorption of the digestion products can keep pace with digestion and the amino acids are never permitted to accumulate in concentrations which reveal themselves to the senses.

Those who are familiar with the numerous attempts to feed mixtures of amino acids to animals for the purpose of securing an answer to some of the questions which have arisen concerning



protein metabolism are familiar with the inherent difficulties in such work. Regurgitation of food and anorrhexia are the never-failing setbacks in such experiments. Mitchell,<sup>6</sup> who made the most elaborate attempt to nourish animals on diets in which protein was replaced by complex mixtures of amino acids, found that after a few days his mice would refuse food rather than consume the diets offered them. When the offending amino acids were left out of the food, the mice would eat the nitrogen-free diet. The best he could do was to feed the amino-acid-free and amino-acid-containing diets on alternate days. From the standpoint of the objective for which the experiments were undertaken, they proved a failure, and apparently solely because of the repulsiveness of the "fully digested" protein (*i.e.*, amino acid mixture) which the animals refused to consume even to the point of starvation. These substances are, however, entirely acceptable when taken in the form of proteins, in which form the digestion products are, as already stated, fully masked.

A similar situation would arise if an attempt were made to nourish either man or animal upon a diet containing glucose as its sole carbohydrate. Glucose is the only sugar with which the tissues are able to deal for the purpose of performing muscular work or for producing heat, and is normally the only sugar found in the blood. Under normal conditions neither humans nor animals take very large amounts of glucose, but, instead, starch is ingested in large amounts daily. This is resolved, of course, during digestion into glucose. One can easily imagine how unattractive the daily diet would be if glucose were made to replace the starch of the food. Starch is tasteless and does not interfere with the appreciation, through the sense of taste and of smell, of the flavors and odors which make certain foods so appetizing. If glucose were the sole carbohydrate in the food, everything would taste sweet, and sufficiently so that all other flavors would be unappreciated. It would probably be impossible for one to take such a diet, even if it were properly constituted with respect to protein and energy content, and with respect to inorganic elements and vitamins. It is not enough that the diet be properly constituted chemically, in the sense that all the necessary complexes and elements are furnished which the body needs for its nutrition. These substances must be taken in the forms provided



by nature so that the unattractiveness of the digestion products will never become detected by the senses.

The fats are another class of foods which are much more acceptable in the form in which they occur in foods of animal and vegetable origin than they would be if contained in the food in the form of their digestion products, fatty acids and glycerol. As an example, butter, which when properly prepared is one of the most palatable of fats, would be wholly inedible if presented to the consumer in the form of the saponified products which can be obtained from it. Especially butyric, caproic, caprylic, and capric acids, which are prominent in butter, are distasteful to the taste and repulsive to the sense of smell. The fatty acids are presented to the intestinal mucose for absorption in the form of soaps. Soaps are, however, so bad tasting that it would be impossible to eat any appreciable amount of them. By their very complexity, the natural foodstuffs are endowed with physical and physiological properties which are of the greatest significance in human and animal nutrition. It is a great fallacy to entertain the idea, which has frequently been discussed by those with little knowledge of physiology, that it is possible or desirable to attempt to nourish the body with predigested foods.

It is of importance, further, that the foodstuffs shall, in the main, be furnished to the alimentary tract in colloidal form, because in this state they have no appreciable osmotic effect. We normally take almost all of our food in the form of molecules so large that they have but an insignificant osmotic value, the only pressure which is exerted within the lumen of the tract being due essentially to the small content of soluble salts and to the sugars contained in the diet. The water we drink contains but little dissolved substances of any kind, except in a few localities where mineral waters abound. The mixture of food and drink which we ordinarily ingest has but a low osmotic pressure as compared to the blood, which contains about eight-tenths of a per cent of sodium chloride.

While it is undoubtedly true that the alimentary tract is capable of secreting dissolved substances against osmotic pressure, and, if time be afforded, of absorbing solutions which are isotonic with the blood, there can be little doubt that, normally, osmosis is an important factor in absorption of soluble material from the

digestive tract. Under the conditions which exist when the foods are principally colloidal, the salt concentration is decidedly higher in the blood and lymph than in the lumen of the digestive tube, and, therefore, the tendency is for water, carrying its low content of digestion products (but exceeding the blood in its concentration in these) to pass through the mucosa toward the blood. The slow rate of digestion of proteins, starches, and fats gives ample time for their removal and absorption in very dilute solution. If the foods were taken in the form of their crystalloidal digestion products they would form a sufficiently concentrated solution to be irritating to the mucosa, and to cause a flow of water from the tissues to the lumen of the alimentary canal. In all probability, such a food mixture constituting a properly balanced meal, but composed entirely of the end products of digestion of proteins, starches, and fats, would possess a decidedly cathartic action because of its irritable properties and high osmotic pressure.

Mention should also be made of the significance of the colloidal materials in the diet and of those contained in the secretions of the alimentary apparatus as an aid to the emulsification of fats. Without emulsification, the fats do not present sufficient surface for the effective action of the lipase, and fat digestion could not proceed in a satisfactory manner in the absence of emulsifying agents. The bile salts and also the carbonates and bicarbonates of the intestinal and pancreatic secretions likewise play an important rôle in this connection as well as do the colloids, especially the proteins.

#### METABOLIC COLLOID PROCESSES IN FOODSTUFFS

Important as is the colloidal property of our principal food substances, considered from the standpoint of their history after ingestion, any discussion of the significance of colloids in the dietary would be incomplete, indeed, if it failed to include the rôle of the colloidal property in the preservation of the foodstuffs which form the basis of the nation's dietary. We may, therefore, turn to a consideration of the rôle of the heterogeneous phase structure in those products employed as foodstuffs.

Foodstuffs of animal origin, such as meats, are preserved by refrigeration, canning in a sterile condition, or are salted sufficiently to protect them against bacterial growth. Meats may, therefore, be regarded as surviving tissue, although they are still undergoing the transformations characteristic of the last stages of dying, since changes due to enzyme action are still in progress. Meats are preserved only in so far as these degradation processes are interfered with. It is quite otherwise with vegetable foods which are preserved in an edible condition during shipment to places remote from production, or are stored over winter as reserve food supplies at the point of production.

Vegetable foods, such as potatoes, turnips, cabbage, fruits, grains, etc., are living things. They are all capable, if taken from the garden, orchard, or field in proper condition, of retaining their vitality over a considerable period, and of developing the following year, or, in the case of the grains, even after many years, a new generation of plants of their kind. When put away under the conditions which experience has shown to be appropriate for their preservation for winter use, they may be kept for considerable periods of time without appreciable deterioration. These conditions are of interest from the physiological point of view. The potato, or any of other products enumerated, is still metabolizing, and it is of the utmost economic importance that it be kept alive during storage. If the tissues stop respiring they would soon be spoiled for food purposes, since dead tissues always undergo degradation processes.

An example of the importance of maintaining external conditions suitable for the continuance of normal physiological processes in fruits and vegetables which are being held in reserve is shown in the study of Bartholomew<sup>7</sup> of the cause of black heart of the potato tuber. A few years ago shippers in the North Central states suffered considerable loss, owing to the development of a black pigment in the heart of the tubers. This could not be detected until the tubers were cut open. If they were kept for a few days before being examined, it was found that a hollow space had formed in the center, due to shrinkage of the dead tissues.

The cause of the trouble was found to be the maintenance of too high a temperature in the refrigerator cars and to insufficient

ventilation. Owing to the danger of freezing in winter, it was the custom of the shipper to place in the center of the loaded cars an oil stove, which was lighted and allowed to burn in the closed car until the oil was exhausted. The burning stove exhausted the oxygen supply from the greater part of the car and likewise brought the temperature up to 38 to 48°, depending on the distance from the stove. The cause of the damage to the potatoes was the acceleration of their metabolic processes by the high temperature, and the exhaustion of the oxygen supply. The potatoes were asphyxiated. As soon as death of the tissues occurred, the peculiar structure was damaged, because the chemical processes in the tuber were thrown out of balance. In living tissues a series of concatenated reactions progress in an orderly fashion, but when death of the tissues occurs, some of these reactions are no longer controlled, but run riot and cause the disintegration of the tissues.

That protoplasm has an organized structure which depends upon the colloidal character of the most essential of its constituents there can be no reasonable doubt. The power of a yeast cell to live and multiply when surrounded by a medium consisting of water, carrying in solution glucose, certain inorganic salts, and ammonium sulfate as the sole source of nitrogen, must arouse the wonderment and admiration of any inquiring mind. It is invisible to the unaided eye, yet it can, by virtue of its peculiar composition and structure, assimilate these simple nutrients and reproduce itself indefinitely<sup>8</sup> and also convert sugar into alcohol, carbonic acid, and water. Under certain conditions it may convert glucose into glycogen and later reconvert this into sugar and ferment it. It may even oxidize alcohol, forming glycerol, succinic acid, and amyl alcohol. The multiplication of the yeast involves the construction of amino acids to the number of 18 or 20, and their arrangement in a definite order in peptide union to form proteins. Such processes are manifestly impossible in any homogeneous medium.

Most biochemists would now agree that there is no such thing as living matter in any sense requiring the possession of attributes other than those resulting from the special manner in which living protoplasm is organized. The peculiar properties of living matter depend upon its unique structure. In the



small space within the yeast cell there is no structure visible which can explain how so many chemical processes can go on simultaneously and at rates which are balanced so that the system is maintained. It is easily conceivable how such a system may be maintained in a heterogeneous system such as is possible where several substances of a colloidal nature participate in its structure. The separate reactions can go on in different phases, and, owing to the intimate relation of both the chemical and physical structures, the individual reactions are effectively prevented from interfering with each other.

The potato, which may serve as an example of vegetable foods generally for our present purpose, is produced by the parent plant for the purpose of bringing forth a new generation of potato plants after a period of weather unsuited for the life of the plant in an active state. The metabolism of the tuber can be greatly reduced so as to conserve food material which is stored within it. If the temperature is lowered or raised, the chemical processes which go on within the tuber respond by proceeding at a slower or a faster rate respectively in a manner comparable with the response of chemical reactions which take place in a test tube.

There is no better illustration of the fact that physical structure as well as chemical composition plays an important rôle in the preservation of vegetable foods than the well-known one of the ease with which physical damage destroys the life, and consequently upsets the chemical equilibrium, of a vegetable tissue. Under favorable conditions the potato can be preserved in good condition for several months. The tuber contains enzymes of several kinds. Amylase, which can digest its starch, and proteases, which can destroy its proteins, are prominent examples. These do not, at temperatures suitable for maintaining potatoes in an edible condition, attack their respective substrates, except at a very slow rate. The potato is constantly giving off carbon dioxide and absorbing oxygen like all other living things. If the physical structure of the tuber is damaged by freezing, however, changes of a chemical nature are initiated which appear to be entirely the result of bringing together enzyme and substrate. The frozen potato quickly becomes sweet. The proteins are digested to amino acids. The structure loses its barriers of

defence against microorganisms and is soon invaded. The potato is rendered unfit for edible purposes within a few hours.

It will be appreciated from what has been said that the colloidal nature of the principal components of our foodstuffs is fundamental to the protection of a reserve supply of many of our most common articles of diet. Without colloids, such as proteins and complex carbohydrates and the complex lipins, our food supply could not be maintained.

Our foodstuffs of animal and vegetable origin are either living, surviving, or dead protoplasm. They all contain within themselves, when unheated, catalytic agents which are capable, under certain conditions of temperature and moisture, of rapidly rendering them easy of destruction by ever present microorganisms. These catalytic enzymes are effectively withheld from contact with the moieties which they are capable of degrading, so that the preservation of food for a time is possible without canning or otherwise destroying the enzymes contained in them. As has been emphasized in the case of the potato, preservation is largely a matter of the effectiveness with which the physical structure of the fruit or vegetable is preserved, which determines the isolation of substrate and enzyme.

The optimal conditions for the preservation of fruits or vegetables, *i.e.*, living or surviving tissues, are the lowest temperatures at which they can be kept without danger of disrupting, through freezing, of the physical structure of their heterogeneous colloidal system, together with sufficient ventilation to permit of continuous respiration by the tissues. Preservation is also made more effective by maintaining a degree of dryness which protects the cortical layer of the vegetable tissue, so that their peculiar physical properties are maintained, and so that bacteria and molds are prevented from growing upon the surface.

It will be seen, therefore, that, with the necessity for providing for a considerable population through the winter season in the temperate zones, and with the necessity for bringing from afar to the more densely populated areas of the world the food products which cannot be produced nearby, the colloidal nature of these food materials is of the most fundamental nature. It makes possible not only sustenance, but the enjoyment of the fruits of many climates and peculiar soil conditions by people

whose food is provided by the perfected methods of transportation of modern times.

In this connection the chemical processes which take place in the ripening of fruits should be mentioned. The ripening of fruits represents a series of changes of a chemical nature which go on in an orderly and regulated rate under suitable conditions. The blossoming of flowers is a comparable process. Both run rather rapidly through a series of digestion processes, accompanied by respiration, which soon causes their physical breakdown and dissolution through the agency of microorganisms. When a tasteless or bitter fruit ripens and becomes sweet, it is evident that the starch, with which chemical analysis shows the unripe fruit to be packed, has in some manner been converted into sugar. This is known to be due to the action of amylase contained in the fruit. Ripening can be deferred by maintaining conditions such that the catalytic action of the enzyme is retarded. But the process does not begin until the development of the fruit has progressed to a certain point, and then takes place too rapidly to suit those who handle such foodstuffs commercially. The difficulty in regulating this process of ripening has been and is a source of great economic loss.

In certain cases, processes for the artificial ripening of fruit which has been shipped in the green and firm condition have been perfected. This is accomplished through the agency of certain chemicals. It has long been the practice of florists to expose buds of flowers to the vapors of anæsthetics such as ether in order to bring them into full blossom weeks before they would normally be ready for commercial purposes. The Arabs have, from time immemorial, hastened the ripening of dates, or have "sweetened up" retarded fruits, by applying cloths moistened with vinegar.

Vinson<sup>9</sup> exposed unripe dates to the vapors of acetic acid for 12 to 15 hours and found that this treatment initiated the ripening process. During this interval the fruit became transparent almost to the seed, and thereafter it ripened in a normal manner. The flavor of the fruit thus ripened by forcing is said to be fully equal to naturally ripened fruit.

Such a method, which is of great value in the marketing of fruits such as the date, which lasts but a short time after fully ripening, may be in many places the factor determining whether



the ripe date can be offered in the market, and in other regions, and whether the cultivation of this drought-resisting fruit can be profitably practiced. It is mentioned here because the process illustrates a case in which a discovery has been made which induces rapid ripening at will of a green, hard fruit which can be shipped without hazard, through initiating, by chemical treatment, a series of changes in the colloids of the unripe date which tends to soften and develop its attractive flavor, through bringing together enzyme and product, the hydrolysis of which it accelerates. If, however, the process of ripening is permitted to go too far before the fruit is eaten, the process of ripening, once set in motion, quickly goes too far. The unripe date may contain as much as 15 to 20 per cent of cane sugar, but soon after becoming fully ripe the fruit is found to contain invert sugar instead of sucrose, and much of its sweetness is lost. Before the ripening process was started, the enzymes which hydrolyze starch and cane sugar, to name but two, were prevented by physical means from coming together. In the normal ripening process there are produced some substances, probably organic acids, which gradually disturb the structure of the heterogeneous system of colloids and bring on ripening.

It will be seen from what has been said in this brief chapter that, both from the standpoint of those processes of nutrition which are initiated with the taking of food, and from the standpoint of the preservation of foods for use out of season, or during transport from distant regions, the colloidal structure is of the greatest significance. Those who think of nutrition only in terms of supplying fuel for conversion into work and heat, and of providing chemical units essential for building the living tissue, take an entirely inadequate view of the process. Satisfactory nutrition demands a preliminary series of preparatory acts which we call digestion, which fit our foods for absorption, and there are deep-seated reasons why this necessitates taking foods in great measure in the colloidal condition.

Economically and physiologically the colloidal nature of foods presents aspects which are worthy of careful consideration. The processes of metabolism are essentially problems of colloid chemistry. Hitherto the field of colloid chemistry has been left too largely to the technical chemists, but it seems certain that in



the near future the physiological chemists must develop a deeper interest in this fertile, though difficult, field of study.

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## CHAPTER XXX

### LEATHER

By

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The manufacture of leather is doubly a colloidal process, since the proteins of which skin is composed are typical organic colloids, and the tannins and most of the other materials used in converting skin into leather are also colloids. It must not be forgotten, however, that the reactions between colloids are still chemical, though their course is often influenced by the peculiarities of the colloid state.

The subject seems naturally to divide itself into three principal sections:

1. The structure and constitution of the skin.
2. The preparation of the skin for conversion into leather.
3. Tanning, the conversion of skin into leather.

#### THE STRUCTURE AND CONSTITUTION OF THE SKIN

**The Structure of Skin.**—It is not proposed to go into a detailed description of the anatomical structure of skin, which may be found in other books. It must, however, be noted that not the whole skin as it exists on the living animal is capable of conversion into leather. The surface layer or *epidermis*, which carries the hair, with the sudoriferous and the sebaceous glands, consists of keratin cells, which are incapable of combining with tannin, or of yielding gelatin on boiling with water, and these must, in most cases, be removed by chemical and mechanical treatment before the actual tanning process. The interior or middle part of the skin, the true leather-producing material, consists almost wholly of white connective tissue fibers composed of collagen, and is completely converted into gelatin by boiling with water. These are, for the most part, arranged in bundles irregularly felted together, but near the outer surface the bundles

become split up into much finer fibrils of only about 1 micro-millimeter in diameter, which are felted to a closer and finer structure. This finer layer is technically called the *grain*, though the term is applied also to the actual outer surface, and is derived from the somewhat grained appearance caused by the skin papillæ. Interspersed with the white connective tissue



FIG. 1.—Vertical section of fresh cow hide (12 diameters). (Kindness of J. A. Wilson).

fibers, but most abundant in the grain layer and in the deeper part of the skin next to the body, and almost absent in its center, is a small proportion of yellow, so-called *elastic fibers*, forming a sort of anastomosing network, which acts as a kind of flexible skeleton to the skin. These fibers are harmless and, perhaps, useful in the firmer leathers and are allowed to remain, but in the softer leathers, and especially in glove leathers, which must

have the quality of "stretch," it is essential that they should be removed. The yellow fibers are almost unaffected by boiling water, which rapidly converts the white fibers into gelatin. They are little affected by dilute acids and alkalies, which swell and even dissolve the white ones, and they do not tan. After liming, they are readily attacked by tryptic ferments, which have little action on the white fibers, and so can be removed. Scat-



FIG. 2.—Vertical section of outer region of cow hide. This shows the sebaceous glands between the hair and *erector pili* muscle, the sweat glands—sausage-like sacs in the center—and a large vein (32 diameters). (Kindness of J. A. Wilson).

tered through the skin are numerous nucleated cells containing fat, and with keratinous walls. In sheepskins these are specially abundant, forming almost a definite layer. There are also blood vessels and the sebaceous and sudoriferous glands, which must be removed from the finer leathers. This takes place in succeeding processes, mainly by digestion with a tryptic enzyme.



**Preservation of Hides and Skins.**—As these are readily putrescible, and often have to be sent long distances or kept for some time before they come into the tanners' hands, some method of preservation must be adopted, which, in both America and Europe, is usually salting. Common salt is only a feeble bactericide, and its effect is largely due to the dehydration which



FIG. 3.—Horizontal section of fresh cow hide. This shows hair and sebaceous glands (135 diameters). (*Kindness of J. A. Wilson*).

it causes. For this reason, the use of even saturated brine is not so effective as that of dry salt. The hides are laid flat and flesh side up in a cool cellar, and heavily strewn with salt; the edges of the outer hides are turned in so as to make a square base for the pile and to prevent brine from running out, and further layers are spread in the same way until the pile is as high as is convenient. After lying for about a fortnight, the hides become thoroughly impregnated with salt, and the pile is taken down, the surplus salt shaken off, and the hides folded and tied in

bundles for transport. It is possible that the strongly dehydrating effect of the salt is at least partly due to the traces of sarcolactic acid naturally present in the hide, producing a degree of "pickling" (*q.v.*), and, if this is the case, the preservation of hides which have reached the ammoniacal stage of putrefaction would be improved by a slight preliminary acid treatment, or by the addition of a little acid sodium sulfate to the salt.

Where salt is dear or heavily taxed, direct drying is often resorted to as a means of preservation, and if this can be done rapidly in the shade it is quite effective and does little injury; but if putrefaction is allowed to take place in the interior of the hide, or if the hide, while still moist within, is exposed to the direct heat of a tropical sun, it is frequently ruined, though it may outwardly appear quite sound.

Various of the modern coal tar disinfectants have been proposed for the preservation of hides, but, unless very cautiously used, most of them are apt to produce a sort of tanning effect which interferes with the later treatment. Alkaline solutions of arsenic are often applied to hides which are to be dried, and are very useful in preventing the attacks of insects, but seem to have no marked antiseptic power.

#### THE PREPARATION OF THE SKIN FOR CONVERSION INTO LEATHER

**Depilation.**—The first chemical stage of leather manufacture is the loosening and removal of the hair and of the epidermis in which it is rooted. The hair is purely a product of the epidermis, though its growing bulb penetrates somewhat deeply into the leather hide, and may be likened to an onion planted on a sheet which is tucked into the soil below, from which it derives its nourishment of blood and lymph. The inner part of the epidermis, the so-called *mucous layer*, consists of growing nucleated cells which multiply by division and have keratinous cell walls which dry and harden as the new cells beneath them force them away from their source of nourishment. The inner living cells are always soft and juicy, and after the death of the animal are easily putrescible. In fact, the primitive method of loosening the hair was to wait for liquefaction by putrescence. This method is to a certain extent still in use for sheepskins, of which the wool is more valuable than the skin, and with care little

damage need be done to the latter, as the hide fiber is somewhat more resistant than the epidermis cells to bacterial action. In America a similar method, called *cold sweating*, was also (and perhaps still is) used to a limited extent for unhairing and finally softening imported dried hides. The action is not a purely bacterial one, for during the putrefaction of the epidermis large quantities of ammonia are evolved, and the writer has shown experimentally that, in an atmosphere charged with ammonia, sheepskins can be satisfactorily unwooled in a few hours,

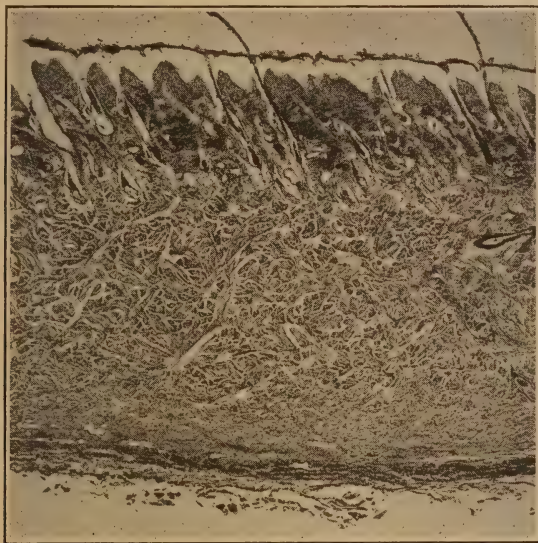


FIG. 4.—Vertical section of calf skin. This is taken from the lime liquor and shows the separation of the epidermis, hair and sebaceous glands from the derma (20 diameters). (*Kindness of J. A. Wilson*).

before there has been time for any serious putrefaction to take place. It has recently been announced by Dr. Ross that the effect is not due to enzymes produced by bacteria, but to one developed by the hide itself after death,—urease,—and that this dissolves in the old lime liquids and gives them their increased solvent power. Generally, the agent now used is milk of lime in pits in which the hides are immersed and turned over from time to time until the epidermis is dissolved and the hair is loosened, partly by the alkaline action of the lime, and, in most cases, partly by the



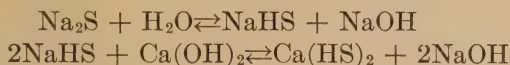
solvent action of enzymes produced by bacteria, many species of which can thrive in a strong lime solution. The process lasts from two to three days to a week or more, depending on the temperature, and on the action of other chemicals which are frequently added to "sharpen" and hasten the action of the lime. The principal one of these is sodium sulfide, but other alkaline sulfides may be employed.

One important quality of lime, which, beside its cheapness, specially fits it for use in this way, is its very limited solubility in water, in which it dissolves only to the extent of about  $1\frac{1}{4}$  g. per liter, and which enables it to be used in large excess without injurious results, while the undissolved portion maintains the solution constantly at full strength. The lime acts on the collagen like any other alkali, forming an ionizing collagenate, but, as Loeb has shown, only swells the hide half as much as its equivalent of soda or potash, since the swelling is due to the osmotic pressure of the ionizing salt, and that of the divalent calcium is only half as much as that of the two sodium or potassium ions to which it is chemically equivalent. The lime dissolves or thoroughly softens the keratinous substances of the epidermis, but, though it swells the collagen fibers, has little solvent action upon them. The solvent action on the keratins is not wholly due to the alkalinity of the lime, but is much increased by the enzymes of bacteria which are always present in used lime liquors, and hence old liquors containing these and ammonia act much more rapidly than fresh ones, but also dissolve more of the collagen and the interfibrillar substance—whatever this may be. It has even been doubted whether lime alone would ever unhair fresh hides in entirely sterilized liquors, for its action is certainly very slow. In the Payne and Pullman unhairing process, in which the hide is first treated with dilute sodium hydroxide, which is replaced by caustic lime in a subsequent treatment with calcium chloride, both solutions being practically sterile, a fresh skin cannot be unhaird without previous treatment in a putrid soak, and the fact has been taken advantage of to lime skins which are to be tanned with the hair on, which remains unloosened.

Sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) when dissolved in water splits at once into 1 mol of sodium hydrosulfide and 1 mol of sodium hydroxide, and if lime is also present the hydrosulfide further



reacts to equilibrium to form calcium hydrosulfide and a further portion of sodium hydroxide:



The action of sodium hydroxide on the hide is similar to that of lime, though swelling it more. The hydrosulfide has but little action on the collagen. Its action on the keratins is little understood, but a strong solution rapidly dissolves hair to a pulp, and weaker solutions have ultimately the same effect, though more slowly, and act first on the softer keratins of the mucous layer. The hydrosulfide gradually disappears from the solution and is replaced by polysulfide, thiosulfate, and such compounds, and the keratins are broken down into simpler forms. The methods for the analysis and control of used lime and sulfide liquors have, however, been recently much improved and we may hope for more definite information in the near future.

As has been stated, concentrated solutions of alkaline hydrosulfides rapidly reduce hair and wool to a mere pulp, and this has been much employed in the unwooling of sheepskins, which are painted on the "flesh" or inner side with a strong solution of sodium sulfide alone or in mixture with lime, and this rapidly penetrates the skin and destroys the hair roots without injuring the wool. The hide, after a thorough washing with soft water (free from carbonic acid, which would convert the lime to carbonate and make it difficult to remove), and, generally, after a slight acid treatment to remove excess of lime, is now ready for tannage into the harder sorts of leather, such as sole and belting leathers, but for the finer and softer sorts it still requires further treatment.

We have spoken so far of liming as a mere process for loosening the hair, but it has also other effects which are desired. The swelling of the collagen fiber bundles possibly ruptures some protective coating which is so thin and transparent that it has not yet been demonstrated microscopically (unless the ligatures of elastin which are found around the swollen fibers are its remains), but in any case it splits the bundles into their constituent fibrils, and so exposes a much larger surface to the tanning agent and facilitates its penetration. This swelling and differentiation

of the fibrils is an essential of all satisfactory tannage, and if hair is removed by processes which do not swell, it is necessary to swell subsequently, and generally with acids, which have a similar effect.

For the softer and finer leathers, excessive swelling is not desired, as it tends to produce a coarse and wrinkled grain surface, and mixtures of sodium sulfide and lime are unsatisfactory because of the powerful swelling effect of the caustic soda. This may be avoided by the use of calcium hydrosulfide made by passing hydrogen sulfide into milk of lime, but as the process is troublesome and rather costly, and the product will not keep if exposed to the air, it has not been much used. A substitute of very ancient discovery, probably introduced by the Moors into Europe, along with the use of alum and several other useful discoveries in leather manufacture, is made by mixing arsenic sulfide (generally the red sulfide) with hot slaking lime. This material is not cheap, and is very poisonous. A cheaper material suggested by the writer may generally be substituted, consisting of a mixture of equivalent parts of sodium sulfide and calcium chloride, the sodium chloride which is formed having no injurious effect.

Further uses of the liming process are to dissolve the hair bulbs, which, when the hair is dark, contain the pigment, and to soften the sebaceous glands so that a large part of them can be forced out of the now open hair pores by pressure with a blunt knife. The lime also, to some extent, saponifies the fat of the fat cells and dissolves their cell walls. While for the firmer leathers short liming and the use of fresh lime liquors only are desirable, for the softer leathers somewhat older limes and longer liming are permissible, the solution which takes place being a partial substitute for that of the next process. It may be taken as an axiom that old limes swell less and dissolve more than fresh ones.

Warm limes also are more active than cold limes, for, although the solubility of lime decreases with temperature, hydrolysis of the collagen fiber increases, and hides unhaird in warm limes make loose and porous leather. On the other hand, very cold limes have but little action on the hide, and a medium temperature of 15 to 20°C. seems best for practical purposes. However, if

the hides after a light liming are plunged or suspended in warm water, the unhairing is greatly facilitated. This is the so-called "Buffalo" method. The temperature may range up to 40 or 45°C., the suspension being shorter as the temperature is higher.

The addition of sodium sulfide to limes not only causes much more rapid loosening of the hair, but induces the hides to swell more than with lime alone. If the sulfide is used in strong solution, however, or by painting, the hide is at first little swollen, owing to the repressive action of the strong salt solution, but, if subsequently suspended in plain water, it will swell, sometimes excessively, and, if the suspension is prolonged, difficulty may occur in fleshing. As this swelling sufficiently differentiates the fiber bundles, subsequent treatment with acid is not necessary for this purpose, though it may be desirable to check excessive swelling and to neutralize the excess of alkali which clings obstinately to the fiber, and cannot be washed out with water alone. During acid treatment, of course, much hydrogen sulfide is liberated.

The causes of swelling in the liming process may be deduced from the general theory of protein swelling as proposed by Procter,<sup>1</sup> and further developed by Wilson<sup>2</sup> and Loeb.<sup>3</sup> The alkali combines with the collagen to form an ionizable collagenate, and the swelling is caused by the excess of osmotic pressure of the ionized base in the gelatinous fiber over that in the outer solution. When the latter is concentrated, as in the case of hides painted with sulfides, the swelling is repressed by the outer pressure until the solution is diluted by suspension in water. Loeb has pointed out that monovalent alkalies like soda must produce double the osmotic pressure, and, consequently, double the swelling of divalent ones, such as lime and baryta, and this is found to be the case in practice. Trivalent bases, such as chrome and alumina, usually do not swell the hide at all, and their collagenates are very stable, so that they are tanning rather than unhairing agents. Thus, the question of swelling is simply one of chemical and

<sup>1</sup> *Kolloidchem. Beihefte*, **2** (1911); and *J. Am. Leather Chem. Assoc.*, **6** (1911), 270; *J. Chem. Soc.*, **105** (1914), 313; PROCTER and WILSON: *Ibid.*, **109** (1916), 307.

<sup>2</sup> WILSON, J. A. and W. H.: *J. Am. Chem. Soc.*, **40** (1891), 886.

<sup>3</sup> LOEB, J.: *J. Gen. Physiol.* (1918) *et seq.*; "Proteins and Theory of Colloidal Behavior," New York, 1922.

osmotic equilibrium, while the solution of the hide constituents is purely chemical and dependent on the character of the constituents. It is largely dependent on their breaking up into the simpler and non-colloid forms of proteoses and amino acids, either by purely chemical means, or through the agency of zymases.

The succeeding processes of preparation, bating or puering, and drenching are largely dependent on these latter agencies, though purely chemical actions also come in, especially in the removal of the lime. For many purposes, and particularly for sole and the heavier leathers, removal of the lime is the only essential, and is readily accomplished by the use of dilute acids. For this purpose, the "weak" or little ionized acids are usually to be preferred, since they can be used in moderate excess without danger of overswelling. The collagen, being amphoteric, is as easily swollen by excess of acid as of alkali, and the consequences are equally unsatisfactory in the actual tannage. Boric acid and organic acids of the acetic and lactic series are mostly in vogue for this purpose, but the stronger mineral acids can be safely used if they are added gradually and their quantity strictly regulated so as not to neutralize quite the whole of the lime, the last traces being removed if necessary by an organic acid, or left to neutralization by the traces of organic acids always present in the tanning liquors. Even sulfuric acid may be used, but hydrochloric is perhaps the most suitable due to the solubility of its lime salt, though care must be taken that it is free from iron which causes discoloration. The principal reason which makes the removal of the lime essential is that it combines with most of the tanning matters, forming products which darken very much on oxidation.

*Puering* and *bating* were formerly almost universally accomplished by fermenting infusions of dog or fowl dungs, the former, puering, being generally used for the lighter leather, and usually followed by *drenching*. Such infusions contain a proportion of ammonia and amine salts, to which a part of their efficacy is due, the lime present combining with the acid and setting free the ammonia or amide, but the principal effect is now known to be due to enzymes produced by fermentation bacteria, mostly of tryptic character, and the whole process has been largely superseded by the use of preparations from the animal pancreas



in conjunction with ammonium chloride to remove the last traces of lime. The tryptic ferments do not rapidly attack collagen, unless it has been considerably altered by liming, but they digest elastin, and probably also the keratins of the cellular tissues, and emulsify fats. Probably in the case of the lighter leathers the removal of the elastic fibers is their most important function. Wilson has shown that in long-continued puering these are completely dissolved.

**Drenching** (much of the exacter knowledge of which we owe to the painstaking work of F. T. Wood, who was also the first to demonstrate the bating properties of the tryptic ferments) consists in treatment with fermenting bran infusions, and is mainly a deliming process, though it also dissolves some of the hide constituents, and, where it follows puering, stops the further action of the tryptic ferments by bringing the skins to a slightly acid state in which such ferments cannot act. The starchy matters of the bran are first converted into glucose by the action of *cerealin*, an unorganized ferment naturally present in the grain, and the glucose then undergoes bacterial fermentation by several types of lactic, butyric, and acetic acid-forming bacteria. As these can only develop in solutions of very feeble acidity, while their action is stopped by the accumulation of their own acid products, the acidity of a healthy drench is automatically self-regulating, and tends to produce a very slight acid swelling of the skins. The hydrogen and carbon dioxide produced float them to the surface, and in the older methods the number of times they were put down again was some indication of the extent of the drenching. This is now no longer available, since the operation is generally carried out in a paddle which keeps them constantly put down. The drenching is judged sufficient by the feel, which should be soft but full, and by the appearance of minute blisters under the grain, caused by the evolution of gas in the tissue. If these are allowed to develop too far, they burst and cause pinholes.

The depleting effect of bates and drenches is due mainly, if not entirely, to their automatically bringing the skin to an acidity near that of the isoelectric point of collagen, which is also its point of minimum swelling. Swelling, however, does not depend simply on the hydrogen ion concentration, but is affected equally

by the presence of neutral salts in the external liquid, which, by their osmotic pressure, oppose that of the ionizing colloid salt to which the swelling is due, and which are always present to a greater or less extent in the drench or bate liquor. The solvent effect of these on the hide constituents is also dependent on the liquid having the optimum hydrogen ion concentration for the enzymes, and both this and the temperature influence the fermentations by which the enzymes and acids are produced. Healthy and active drenches have a slight swelling effect, and are, therefore, always slightly more acid than the isoelectric hydrogen ion concentration, while pueres and bates, though perhaps slightly acid when the skins are introduced, become decidedly more alkaline from the lime introduced with the skins, and this is necessary to their action, since the tryptic ferments on which they mostly depend for their efficacy can act only in an alkaline medium. The isoelectric point of collagen is about pH 4.7, or  $n/50,000$  acid, but that of active bates is always of higher pH or more alkaline. Wood<sup>4</sup> found the average of several puer liquors to be pH 5.32 before use, and 71.2 after use. It may seem singular that the maximum depletion of skin can thus occur decidedly on the alkaline side of the isoelectric point, but while this alkalinity is necessary for the proper action of the zymases, it will be seen that the swelling curve of gelatin (and collagen), while it rises very rapidly on the acid side of the isoelectric point, does so only slowly on the alkaline side, so that a small divergence does not materially increase the swelling.

In former times bating of the finer leathers was invariably done with fermenting infusions of dungs, dog dung for the finest and thinnest leathers, and pigeon or fowl dung for the somewhat thicker ones. In 1895 a patent was taken by Drs. Popp and Becker for the use of special bacterial cultures, in conjunction with a preparation to make a suitable culture medium. A mixed culture, mainly of bacteria of the *coli* type, was found most effective, and the culture medium was produced by digesting hide fleshings with an acid, and drying the product. As Wood in England had taken a very similar patent, it was decided to work the two in conjunction, and an artificial puer, "Eroding," was put on the market and rather extensively used. For certain classes of

<sup>4</sup> "Puering, Bating and Drenching," p. 79.

leather this proved very effective and decidedly safer than natural puer. Previous to this, Wood had shown that a pancreas extract had marked puering properties, but had neglected its development in favor of erodin. Such an extract is now prepared and placed on the market by Dr. Röhm under the name of "Oropon," with the improvement of the addition of a definite quantity of ammonium chloride, which was found necessary to reduce the amount of free lime in the skins and to activate the trypsin. This has proved extremely successful and has largely replaced the use of dung bates. Wood already had an American patent covering the use of pancreatin (trypsin) and, with the advent of the recent Great War, he was able to acquire from the English Government the use of Röhm's English patent, and a preparation is now manufactured under the name of "Pancreol," which is identical in principle with "Oropon," but somewhat improved in preparation. While for most leathers these pancreatin preparations have proved perfectly satisfactory, there are still some, such as glazed chrome goat, for which the natural dung puer is still in use. It has been shown by Wilson and others that one of the principal effects of the trypsin is the digestion and removal of the skeleton of elastin fibers which prevent the stretching and smoothing of the grain in goat and sheepskins, while it has but little effect on the white collagen fibers.

**Pickling** is a process which has been long in use for the preservation of sheep pelts and split grains for transit and storage, and now frequently as a preparatory process, where it is desired to introduce acid into the skin without swelling. It is in many ways so remarkable that some 25 years ago it attracted the writer's attention as an important subject for investigation, though it was not until 1911 that he was able to give a rational explanation of its causes, and then only an incomplete one. In 1914 a second paper was published in the *Journal* of the London Chemical Society which cleared up most of the doubtful points, and in 1916 a paper in the same journal by J. A. Wilson and the writer placed the theory practically in its present form. Since that time it has been confirmed and extended by J. Loeb, and by Wilson himself, and is now generally accepted in America and England, though in Germany many chemists still adhere to the older theory which claims that the phenomenon of "pickling" is one of adsorption or



surface attraction. The Procter-Wilson theory, however, not merely gives an intelligible explanation based on known chemical laws, but, if the valency and combining equivalent of the protein are known, enables the curves of acid absorption and swelling to be calculated with an accuracy agreeing with observation within the limits of experimental error.

The oldest and simplest form of pickling was, in the first place, to swell the skin with dilute sulfuric acid, and then to "pull it down" in a saturated solution of common salt, after which it could be drained and kept in a wet condition an almost unlimited time without putrefaction. In modern practice a certain amount of salt is generally added to the "rising" solution to control undue swelling, and the pickling can be done in a single solution of salt and acid. Wilson states that a solution about 0.05 *N* of either sulfuric or hydrochloric acid, and about 12 per cent of common salt is satisfactory, but in England, if the skins are to be exported or kept for a length of time, they are usually finally treated in a saturated solution of salt. Any acid such as formic, of sufficient "strength" to swell the skins, may be used with equal effect and other chlorides might be substituted for that of sodium. When this treatment is applied to thin sheets of gelatin they are so far dehydrated as to become quite hard and horny.

The theory of the process is given more fully in another section of the book,<sup>5</sup> but for the sake of clearness must be briefly recapitulated here. Collagen, being amphoteric, combines with either acid or alkali according to whether the hydrogen ion concentration of the external solution is above or below its isoelectric point, but as the protein is very weak, either as acid or base, the salt is largely hydrolyzed, and no point of definite saturation can be reached, as would be the case with a "strong" base and "strong" acid. The change is a gradual one, and, theoretically, actual saturation occurs only when the acid or alkali is at infinite concentration. Confining our attention to the acid salt, which was first investigated, we find that collagen chloride is freely ionizable into  $\text{Cl}'$  and a colloid cation, but the latter from its nature is incapable of diffusion outside the jelly mass, while the  $\text{Cl}'$  is also retained within it by the attraction of the ionized base. As the jelly is freely permeable both to the hydrogen ion and the anion

<sup>5</sup> Cf. Chaps. I and II.



of the external acid, it results that it contains an excess of  $\text{Cl}'$  and a deficiency of  $\text{H}^+$  equivalent to the ionized base by which the  $\text{H}^+$  is repelled. In equilibrium, as Donnan<sup>6</sup> has shown, the *product* of the concentrations of  $\text{H}^+$  and  $\text{Cl}'$  in the jelly must be equal to that of the same ions in the external solution (where they are necessarily equal to each other). The osmotic pressures in the jelly and the outer solution are, however, equal to the *sum* and not to the product of the ions which they contain, respectively, and, as the sum of unequal numbers is always greater than that of equal ones giving the same product (as the sides of a rectangle are longer than those of a square of equal area) there must be an excess osmotic pressure in the jelly over that of the outer solution, and it is this excess which causes the swelling. As the osmotic pressure in the jelly is always greater than outside, this swelling would go on to infinity and solution if it were not opposed by the cohesion or internal attraction of the jelly itself; but it can be shown that this cohesion obeys the ordinary law of elasticity (Hooke's law) and increases with the extension, so that a point (that of maximum swelling) is reached where the osmotic pressure is balanced by the cohesion. As the cohesion is diminished with rising temperature, the maximum swelling increases, and at a certain temperature (for gelatin about  $30^\circ\text{C}.$ ) goes on to infinity and solution. As the quantity of collagen or gelatin present is limited, and can only combine with a given quantity of acid to form ionizable salt, the addition of more acid does not increase the internal excess pressure, but lessens the proportional difference between the two. The maximal swelling is reached, therefore, with a very small concentration of acid (about pH 2.4 of the external acid, or pH 3 of the jelly itself) and any excess tends to diminish it. The same effect is produced by the addition of neutral salts which increase the osmotic pressure both in the outer solution and in the jelly, and so lessen the proportional difference between the two, so that with either increased acid or neutral salt the swelling rapidly diminishes through the internal cohesion of the jelly. It is probable, however, that the cohesive attraction is not the only force which leads to the extreme dehydration which takes place in strong salt

<sup>6</sup> DONNAN and HARRIS: *Trans. Chem. Soc.*, **99** (1911), 1554.

DONNAN: *Z. Electrochem.*, **17** (1911), 572.

solutions. There is much reason to believe that matters in solution combine with the solvent to form something of the nature of hydrates, and that the water so combined is incapable of acting at the same time as a solvent for other matters, so that water is actually withdrawn from the jelly by the superior attraction of the salt. For instance, the addition of potassium carbonate to wine will actually separate the alcohol in a tolerably concentrated form as a distinct layer, and most proteins are precipitated from their solution by addition of sufficient of a soluble neutral salt, such as magnesium or ammonium sulfate. A saturated solution of ammonium sulfate or potassium carbonate will so far dehydrate the fibers of raw pelt as to prevent their adhesion, so that, on drying, the skin remains as a porous and flexible, though really untanned, leather. A similar effect, as shown by Knapp, is produced by absolute alcohol.

#### TANNING: THE CONVERSION OF SKIN INTO LEATHER

Professor Knapp, who may be considered the father of leather chemistry, in his doctorate thesis in 1858 showed that the essential difference between pelt and leather is that, in the latter, the fibers are no longer in the condition of a colloid jelly, but may be dried without adhesion, so that the skin remains porous and flexible. He obtained this result by treating the pelt with alcoholic solutions of gradually increasing strength, finishing with absolute alcohol or a mixture of this with ether. This solution penetrated the interstices between the fibers, depriving them of water, so that they ceased to be sticky, and could be completely dried without adhesion. The material obtained in this way was white, porous, and flexible, and had all the outer characteristics of a white leather, but on soaking in water returned completely to the pelt condition. Knapp further found that the addition of a trace of stearic acid to the absolute alcohol delayed or prevented this reversion by coating, and to an extent waterproofing, the fibers, so that water could no longer be readily absorbed. He concluded from these experiments that dehydration without adhesion was the essential characteristic of tanning, and that the action of tanning materials was simply so to coat the fibers that they should be non-absorbent of water and capable of being dried without adhesion to each other. The operation appeared

to be a purely physical one dependent on the power of extended surfaces to fix dissolved matter upon them, which has since been called *adsorption* to distinguish it from the absorption which takes place throughout the substance of the absorbent. Willard Gibbs many years ago showed that dissolved substances which lowered the surface tension of a liquid must necessarily accumulate at that surface, and this fact has been applied by advocates of the adsorption theory to explain all sorts of accumulations on surfaces in ways which Gibbs never contemplated. Most of these phenomena can be approximately represented by a mathematical formula of the form of  $w = ax^b$  where  $w$  is the amount of solute removed from solution by unit weight of the absorbing material,  $x$  the final concentration of the solute, and  $a$  and  $b$  are constants selected to suit the occasion, and which may vary very greatly. Such a formula can approximately represent almost any reaction which begins rapidly and diminishes as it proceeds, but in the case of adsorption it has absolutely no theoretical justification. However, where  $b$  is the fractional relation of the molecular weight of a substance which dissolves with different molecular weight in two immiscible solvents, it will represent the distribution of the dissolved substance between the two. This would rather favor the idea that the phenomenon was one of partial *solution* in the surfaces (as no doubt it sometimes is) than of real surface adsorption. A further confusion of thought is shown in calling the curve so calculated an "adsorption isotherm," since an isotherm is a curve of equal heat, and has nothing to do with the concentration of solutions. That fixation of dissolved substances on surfaces is a real phenomenon there is no doubt, and the adsorption of many substances by finely divided charcoal is a familiar instance, though it occurs in many cases where no twisting of the Gibbs theorem will account for it.

The effect of stearic acid in rendering alcohol leather more resistant to water, observed by Knapp, is not an isolated phenomenon, and similar results are obtained with various substances which it is almost impossible to suppose can produce adherent coating of the fibers. Thus the leather produced by the dehydrating action of potassium carbonate is rendered permanent by the addition of a small quantity of formaldehyde, and the writer has found that a dehydrated leather produced by a saturated solu-



tion of ammonium sulfate, which, when the pure salt was used, returned readily to pelt on soaking, was quite permanent and resistant to water when made with the ordinary commercial salt containing traces of tarry or phenolic matters. Pickled skins, when dried out, form a white leather which at once swells and becomes pelt in water, but a light tannage in salted vegetable liquors, or a moderate treatment with alum or chrome salts or with formaldehyde, will render it permanent. The ordinary alum tannages are, in fact, such leathers. Alum or aluminum sulfate alone will not produce a practical leather, and it has been known from almost prehistoric times that the addition of salt was necessary in order to do so, but the real function of the salt long remained a puzzle. It was suggested that the chloride and not the sulfate was the tanning agent, and that the salt reacted with alum to produce it, but aluminum chloride proved as incapable alone of producing a good leather as the sulfate. What really happens is as follows: Aluminum sulfate or alum hydrolyzes in solution forming sulfuric acid and aluminium hydroxide, which is a very weak base. The sulfuric acid thus set free swells the pelt like the rising liquor in pickling, while the addition of salt serves the same purpose as it does in the latter case. Alumed leather is, thus, at first largely merely pickled, and very readily loses much of its tannage in water, but, by "aging" for a few weeks, some further change takes place, and it becomes much more permanent. Exactly what happens is not yet quite clear. As the pelt combines with the acid of the sulfate, the hydrolysis proceeds further, and, since the normal sulfate can exist in solution only in the presence of free sulfuric acid, more basic sulfates are formed which are less soluble in water and combine more firmly with the pelt. Whether actual chemical compounds are formed, or precipitation is effected on the surface of the fiber, is by no means fully proved, though recent investigations rather favor the former view. On the other hand, it has been shown that very finely divided insoluble powders, such as ultramarine, can convert pelt into leather by mere mechanical drumming, and most colloid suspensions seem capable of producing leather.

Chemically normal salts of aluminum, chromium, and iron are always acid in solution from hydrolysis, as has been explained, and are also capable of dissolving a further portion of the hydrated



oxides, or a part of the acid of the normal salt can be neutralized by an alkali without precipitation. Such solutions are spoken of as "neutralized" or "basic," and in some few cases an actual basic salt of definite composition can be crystallized, but mostly the proportions of base and acid are quite indefinite, and they can be viewed with equal probability either as mere solutions of the excess base in the normal salt, or as a mixture of various basic salts, in which a portion of the acid is combined with OH instead of with the metallic base, though it is rarely that any definite formula can be assigned. In any case, however, these basic solutions have definite and characteristic properties. If the neutralization is carried to its extreme limit, they become unstable, and are often precipitated by boiling or even by dilution, and appear to be rather colloidal suspensions than true molecular solutions, and in many cases will not pass through a colloidal membrane. If ferric chloride be allowed to dialyze into distilled water through a parchment paper membrane, the chlorine will pass through into the external water, while the iron will remain in the dialyzer until merely a trace of chlorine remains. The solution becomes dark brown in color, and deposits iron oxide either on dilution or on boiling, and was at one time advertised as a tonic under the name of "Fer Bravais."

These basic or partly neutralized solutions find a useful employment in leather manufacture. Having a largely reduced acidity, they can be used in tanning without the addition of salt, but if too basic, the further abstraction of acid by the pelt itself leads to their precipitation, and the liquor becomes turbid, an effect which is often observed in basic chrome solutions. This tendency to instability, if not carried too far, is a useful one, since it enables the pelt to absorb a larger proportion of the metallic salt, but successful tanning is much dependent on its proper regulation. With the normal salt, practically only the base equivalent to the acid which the skin can take up can be absorbed, and, though this quantity can be somewhat increased by the free use of salt, which enables the combination of acid to be carried almost to saturation without undue swelling, the quantity is a small one in proportion to the weight of hide substance, and the tannage can only be a light one. By neutralizing a portion of the acid of the normal salt, a much larger amount of

the base can be taken up before the limit is reached, and from the instability of the basic salt, fixation of its base can go on gradually, even when the skin can absorb no more acid. Thus the normal salt, being crystalline and in molecular solution, penetrates very rapidly, while the basic salt, being probably colloidal, penetrates very much more slowly, but gives a much fuller tannage.

**The Basic Chrome Tannage.**—The most important application of these principles is to basic chrome tannage, though they are also applicable to alum, and to a certain extent to iron tannages. It is a singular thing that, though the first really successful chrome tannage was that invented by Augustus Schultz in 1884, a perfectly practical basic tannage was described by Knapp in 1858, but was never developed further, since Knapp did not discover that it had any real advantages over the common alum tannage, while it was more expensive. Schultz's tannage was somewhat different in principle, the chrome being introduced into the leather as chromic acid from an acidified bichromate solution, and reduced in the fiber by acidified sodium thiosulfate, which also rendered it somewhat basic. In 1893 Martin Dennis, in order to get around the Schultz patent, revived Knapp's old process, patenting it almost in the words of Knapp's thesis. He made his liquors, however, by dissolving chromic oxide in hydrochloric acid and subsequently rendering this more basic by the addition of caustic soda, under the supposition, which has already been mentioned with regard to alum, that only the chloride and not the sulfate was a satisfactory tanning agent. A little later it was shown by the present writer that good liquors could be made directly from bichromate in the presence of enough hydrochloric acid to leave the solution basic, and, shortly after, that equally good results were obtained with sulfates, and that chrome alum itself made a good tanning liquor when made basic with sodium carbonate. The writer advised glucose as a reducing agent, and the glucose liquor has been largely and successfully used, but many other substances, and especially other carbohydrates, can be used for the purpose. J. B. Blockey has patented a very satisfactory liquor made by boiling the suitably acidified bichromate with excess of spent tanning material, which is left in the vat until entirely oxidized and dissolved, more being added as required. A very useful method was invented by Balderston

in the United States, and by more than one other chemist independently in England, which consists in the reduction of a strong solution of sodium bichromate directly with sulfur dioxide produced by burning sulfur. Sodium bichromate is so soluble that a concentrated chrome liquor can be prepared at once, and diluted as required, and sulfur dioxide is so weak an acid that for many purposes the liquor is sufficiently basic. The presence of an excess of acid renders the penetration very rapid and prevents any tendency to the precipitation of insoluble basic salt.

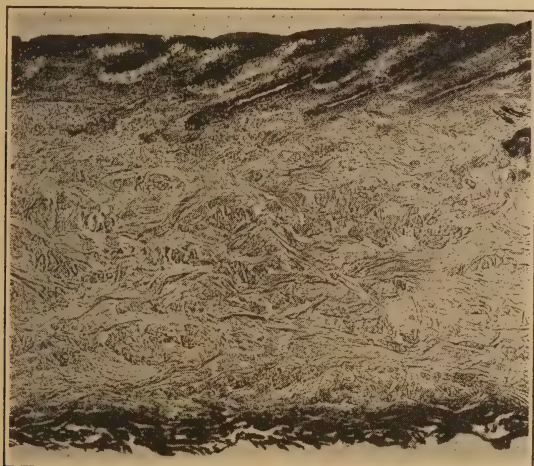


FIG. 5.—Vertical section of chrome tanned calf skin (40 diameters). (*Kindness of J. A. Wilson*).

Though the direct basic process of chrome tanning has for many purposes quite superseded that of Schultz, the latter is still almost universally employed in the manufacture of glazed chrome goat, though the reasons why it proves superior to the direct basic process are not quite clear. One explanation is that, during the reduction in the Schultz process, a considerable quantity of colloidal sulfur is liberated from the thiosulfate and is taken up by the leather, giving it a softer and a fuller tannage. To a certain extent this effect can also be obtained in the direct basic process by using a solution of thiosulfate or of a polysulfide for the neutralization of the still acid leather. Purely sulfur leathers can be produced by treating a merely "pickled" skin in the



same way, but the sulfur does not seem so intimately combined with the skin as when it is liberated gradually in the process of tannage.

**Neutralization.**—In whatever way the chrome tannage is accomplished, the skin will be left in a somewhat acid condition, and if it be washed immediately, a considerable quantity of chrome salt will be washed out and wasted (though in basic tannage a further fixation takes place by “aging” for a few hours in the wet state). To prevent this, and to complete the tannage, it is necessary to bring the skin into a nearly neutral condition by a weak alkaline solution, but considerable care is necessary in doing this, since, if the skin be made actually alkaline, it dries hard and peltly, and the tannage seems to be destroyed, though the chrome salt still remains.

The neutralization is generally followed by *fat liquoring*, which consists in drumming with a weak emulsion of some oil (free from hard fatty acids) and a little soap, or sometimes a sulfonated oil. Dyeing may take place either before or after fat liquoring, according to the dyes used. If the neutralization is not thorough, the fat liquoring is best done immediately after neutralization before the more acid liquor in the interior has time to diffuse to the surface, where it sometimes curdles the fat liquor.

The theory of chrome tannage will be further discussed in conjunction with that of vegetable and other tannages.

**Vegetable Tannage.**—The oldest, and still the most important, way of converting skin into leather is by soaking it in infusions of barks, fruits, or galls which contain members of the class of compounds known as *tannins*. Though many, or perhaps all, of these bodies are colloids, it would not be suitable here to discuss their detailed chemistry which, in most of them, is far from completely understood.

The current way of estimating tanning matters in tanning materials is by what is really a tanning experiment on a small scale and under rigidly prescribed conditions. A dilute solution of the tanning substance is shaken with a prescribed proportion of moist and carefully purified hide powder which previously has been rendered still more insoluble in cold water by a light chroming with a basic chrome salt. Equal volumes of the solution, after allowing for the water carried in by the moist hide powder,



are evaporated to dryness, and the difference in weight of the residues gives the amount of matter absorbed by the hide powder. The method is only an empirical one, but if carried out with all the precautions which have been prescribed by the American Leather Chemists' Association or the European Society of Leather Trades Chemists, which differ only in unimportant particulars, it gives highly concordant results. Most tanning infusions contain, beside tannins, which are entirely taken up by the hide powder, varying quantities of phenolic bodies, such as gallic

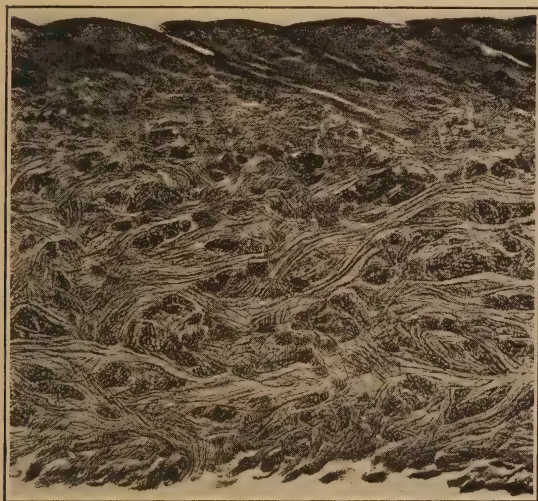


FIG. 6.—Vertical section of vegetable tanned calf skin (40 diameters). (*Kindness of J. A. Wilson*).

acid, which are only partially and more loosely absorbed. The proportion of these bodies which remains unabsorbed is generally known as *non-tannins*, and is usually supposed to be of no value to the tanner, but the separation is by no means so rigid as might be desired, and Wilson and Kern<sup>7</sup> have tried to make it more so, by thoroughly washing the tanned hide powder, and determining its gain in weight after drying. They have shown that a very considerable part of what is at first absorbed by the hide powder can be removed in this way, and that what remains

<sup>7</sup> WILSON and KERN: *J. Ind. Eng. Chem.*, **12** (1920), 465, 1149; **13** (1921), 772; **14** (1922), 1128.

is irreversibly fixed. They propose to call this the "true" value of the tanning material. It has, however, been shown by Meunier<sup>8</sup> that, although these phenolic bodies are not capable of tanning directly, they become so by oxidation, and are largely fixed in the leather by exposure to air in drying, so that their tanning value is still *sub judice*, and it may be questioned whether Wilson and Kern's method really gives a closer approximation to commercial value than that ordinarily in use, though it is unquestionably a valuable addition to our scientific knowledge.

Normal tannage can apparently take place only when both the liquors and the skin are on the acid side of the isoelectric point of collagen, pH 4.7, though it has been shown that gelatin solutions are precipitated by tannin up to a pH of about 8, which is decidedly alkaline. Most tanning infusions are naturally acid, either from phenolic acids already present, or from those of the acetic and lactic series from bacterial fermentation, but often insufficiently so, since with modern rapid tannage there is not much time for fermentation, and apparently a larger proportion of acid is needed with stronger liquors. It is absolutely necessary, for the production of satisfactory leather, that the fiber bundles of the collagen should be swollen and the fine fibrils differentiated at some stage of the process, and, if this is not done in liming, it must be done by acids, either before or during tannage. To make firm sole leather, the fiber must be tanned in a moderately swollen state, while for soft leathers the less it is swollen at the time of tannage the better, so long as it is on the acid side of the isoelectric point. This corresponds with what has already been said about the preparation of the hides or skins. For soft leathers the collagen is brought to a flat and depleted state by bating and drenching, and a minimum of acid supplied in the liquors, while for sole leathers every effort is made to maintain the plumpness due to liming, and gradually to replace the alkaline with acid swelling, either in the liquors, or sometimes by a previous treatment with acid. At the same time, the strength of the tanning liquors is very gradually increased to avoid a too rapid tannage of the surface, which would not only lead to a wrinkled "drawn" grain, but to a surface-hardening which would render difficult the subsequent tannage of the center. For this purpose

<sup>8</sup> MEUNIER: *Collegium*, 7 (1908), 195; 8 (1909), 58, 319.

old liquors which have already been used on previous packs of hides are to be preferred to those freshly made, since they contain a larger proportion of mildly astringent phenolic matters, and act much more gradually. After the surface is colored and the hide partly tanned through, the strength of the liquors may be gradually increased, and, when thoroughly tanned through, the hides, especially for sole leather, are frequently "laid away" in the strongest infusions which can be prepared, and often with an addition of solid ground tanning material. During this part of the process the leather gains in weight and firmness by the deposition of solid matter (ellagic acid with pyrogallol, and "reds" with catechol tannins) on and between the fibers.

At the conclusion of the process, sole leather is frequently *bleached*. In America this is usually done by treatment with sulfuric acid, sometimes preceded by a treatment with a soda solution to redissolve the surface reds; in England, by so-called "bleaching extracts," which are light-colored extracts, heavily treated with sodium bisulfite, or now frequently with synthetic tannins. In either case the bleaching lessens the weight and water resistance of the leather, and serves no useful purpose except to make it more attractive to the eye in the rough, while on the boot it is almost invariably covered by a pigment "fake." Sole leather is now lightly oiled, partly dried, or wholly dried and damped back, and smoothed by rolling under heavy rollers; or sometimes, in England, also by "striking out" by a machine. This was formerly done by hand with a two-handled tool of triangular section called a "striking pin," or by scouring with stones and brushes. Dressing or lighter leathers for harness or for the uppers of boots are subjected to the further process of *currying*, which is largely mechanical, but, so far as it is chemical, consists mainly in impregnating the leather with fats and oils. The lightest leathers, such as moroccas, are dyed, lightly oiled, and subjected to a good many mechanical processes, such as shaving, graining, and glazing.

Beside purely vegetable tannages, "combination tannages" are made, partly vegetable and partly mineral tanned, alum and basic chrome being the mineral tannages most frequently combined. These may be taken in either order, the



tannage which is applied first having in general the greatest effect on the character of the leather, though this is also influenced by the extent to which each is carried. "Semi-chrome" is mostly made from Indian sheep and goat (so-called "Persians"), by partly stripping the vegetable tan by drumming with alkaline solutions, and then giving a basic chrome tannage. Leathers can thus be made which have all the appearance and many of the qualities of genuine chrome. Vegetable tannage cannot be followed by the Schultz chrome process, since the bichromate solution oxidizes and destroys the vegetable tan, and renders the leather peltly, but chrome tan by either process may be followed by vegetable tan, though care must be taken not to overtan, which makes the leather tender.

In former days the leather was mostly tanned with oak bark which, in the case of the common European oak, contains a natural mixture of catechol and pyrogallol tans, and deposited on the leather a good deal of "bloom" (ellagic acid), especially as the tannage was a slow one. This bloom had to be removed from the surface by scouring with brush and stone, the leather was at the same time freed from the usual wrinkled grain by the same operation, and was shaved to the required thickness. It was then uniformly damped, and coated on the flesh side, and sometimes on both sides, with a thick layer of "dubbin," and hung up to dry slowly. "Dubbin" was a mixture of cod oil and tallow, in proportions somewhat adjusted to the temperature of the drying room, so as to remain in a pasty state on the surface of the leather. As the moisture dried out, the liquid part of the "dubbin" gradually took its place by capillarity, and the leather became uniformly saturated, according to the quantity applied, the harder part of the fats remaining on the surface as a white layer, which was removed by the slicker (a smooth-edged plate of steel with a handle at the back) as "table grease," and usually remelted with a fresh lot of "dubbin." The principal use of the harder fats was thus simply to bring the "dubbin" to a suitable consistency to remain on the surface and retain the liquid part, without either running off or becoming so hard that it could not be absorbed.

In these days speedier methods are used. The prepared and damped leather is placed in a heated drum, run a short time to



acquire the temperature, and the suitable quantity of melted grease, often consisting largely of hard fats, is run in through a hollow axle, and the drum revolved for perhaps 20 minutes, when practically the whole of the grease is absorbed. The drum is then run open, or with a current of cold air for cooling, the leather pulled out on the floor, and, as soon as it is cool enough to handle, is spread on the table, and the surplus grease removed with the slicker. It is then hung up to dry. When the writer was in America 30 years ago, it was not uncommon to weigh out 100 per cent of hard grease on the dry weight of the leather for "glove grain," and it all went in! He actually extracted 45 per cent from finished leather, and, though it was dark brown as it came from the drum, it took a bright color when boarded up to break up the hard grease. Whether the same practice holds today he cannot tell, for much alters in 30 years. At the same date in England it was quite common to drum in powdered barium sulfate with the grease, simply to weight the leather, but the practice has quite gone out since the advent of the leather chemist as much too easily detected. The writer once found  $\frac{1}{4}$  per cent in a leather intended to be pure, but stuffed in a dirty drum! About 16 per cent of grease is all that can be gotten in by the old-fashioned hand stuffing. Leather of this sort is usually finished on the flesh side by what is called "waxing" with a composition of oil (or in the States, of soap) and lampblack, followed by sizing, but many leathers are finished on the grain by dyeing, and by "boarding up" to raise a "grain," or commonly by embossing with an engraved roller, or sometimes with an electrotyped plate in a press to imitate some natural grain, such as goat, pigskin, alligator, or "camel." These vegetable tanned leathers have, however, been largely replaced by chrome and chrome combinations.

**Theories of Tannage.**—Historically, the earliest theory was that of Sir Humphrey Davy, who investigated the precipitation of gelatin by tannins, and viewed it as a simple chemical combination, but with the advance of chemistry and Dalton's discovery of combining proportions, it fell into disrepute, since no definite and constant stoichiometrical proportion could be proved. Probably the next important theory was that of Knapp (1852), who showed that a material having most of the physical charac-

teristics of leather could be produced from raw hide by simple dehydration with absolute alcohol in such a way that the water was removed without allowing the fibers to adhere together, and, although this alcohol leather reverted to a raw condition on soaking in water, a good deal of permanence could be given to it by the addition of a little stearic acid to the alcohol, which coated, and, to a certain extent, waterproofed, the fibers and prevented their adhesion. Knapp tried many important experiments on various sorts of tanning, and among others discovered a perfectly practical method of chrome tannage, which was not used only because its value was not appreciated. In place of developing chrome, he unfortunately devoted much time to an iron tannage, but without much success, and it is doubtful whether iron tannage can ever prove of commercial value under ordinary conditions, though, owing to the scarcity of chrome in Germany during the war, a good deal of attention was paid to it, and some fairly satisfactory iron-and-chrome combinations were produced.

Knapp's theory of the purely physical nature of the combination in tanning has remained the popular one in Germany, where it has been strongly supported by Wo. Ostwald and others, and considered as a case of "adsorption," whatever that may be, but a view has gained ground in America and England that the change is of a colloidal character, and dependent on the opposite electric charges of the hide fiber and the tannin particles, which combine and electrically neutralize each other. Recent investigations by R. J. Browne at the Procter Research Laboratory at Leeds go far to prove that all vegetable tannins are colloidal in character, since they can be entirely removed from solution by ultrafiltration, and it is known from cataphoresis experiments that they are negatively charged, while hide fiber on the acid side of its isoelectric point has a positive charge in consequence of the Donnan equilibrium. If two colloid suspensions of opposite charges come in contact, they combine, much as two oppositely charged ions would do, and, if mixed in the right proportions for complete neutralization, the precipitation is complete. The Procter-Wilson theory of tannage holds that leather is such a combination, and with regard to what may be called the first stage of vegetable tannage there is strong evidence in its favor. Tannage only takes place when the hide fiber is slightly swollen with acid

and so possesses a positive Donnan charge, and this charge will naturally vary with the difference between the hydrogen ion concentrations of the pelt and the liquor which is in equilibrium with it, which is greatest when the acidity is very small. In alkaline liquors, tannage does not take place. This seems a perfectly satisfactory explanation of actual combination of tannins and hide, but if, as in sole leather tannage, the leather is allowed to remain for long periods in liquors which contain precipitable matters like ellagic acid or phlobaphenes (so-called "insolubles"), a further deposition takes place on the fiber which adds to weight and solidity, and which is probably of the physical character which has been called "adsorption." The bodies which are deposited are usually all colloidal suspensions, or become so by fermentive changes in the liquors. They are easily liable to flocculate or precipitate in the liquors themselves, and very slight attractive forces will determine their fixation on the surface of the fibers. This sort of secondary tannage takes place only in the presence of these difficultly soluble bodies, and does not seem to occur when only the more soluble tannins, such as gallotannic acid, are present. (A similar effect takes place in chrome tannage with very basic liquors, and a piece of leather, which by accident had been repeatedly tanned by the Schultz process, became completely mineralized like a bit of green tile.) Many substances, however, occur in liquors, which, in their unaltered condition, are "non-tannins" and not absorbed permanently by hide, but which undergo changes which give them tanning properties. An instance of this is catechin, which is largely found in gambier, and other catechus, as a crystalline substance without tanning properties, but which is converted into catechutannic acid by dehydration on boiling. Meunier has also shown that gallic acid and other phenolic acids produce tanning substances on oxidation, and this is particularly the case with hydroquinone with which he has produced leathers of remarkable permanence.

Formaldehyde tannages seem to belong to a quite different class from the vegetable ones of which we have just spoken. Formaldehyde is in no sense a colloid, and it apparently tans most readily in alkaline solution. It has the power of conjugating with a great variety of other compounds, and it probably does so



with collagen, forming a body insoluble even in hot water, but it does not cease to exist as formaldehyde, and can be quantitatively recovered from the formaldehyde leather by digestion with dilute hydrochloric acid. Meunier<sup>9</sup> considers that the importance of the alkaline carbonate used in formaldehyde tannages depends entirely on its dehydrating power, but of this the writer is not fully convinced.

Meunier's experiments with bromine and with hypobromites and hypochlorites as tanning agents<sup>10</sup> give rise to somewhat similar considerations. None of these substances are colloids, and none of them can give rise to a coating of the fiber, but evidently act simply by making the dehydrated fiber insoluble and non-adhesive by producing some actual chemical change. Chrome tanning is another case which at the present cannot satisfactorily be explained on the basis of colloidal behavior, though it seems probable that the basic chrome liquors are at least partly colloid, and it has been shown that some chrome compounds take a negative charge, but the fixation of chrome does not seem confined to these. There also seems some reason to think that both chrome and alum combine with collagen as bases, though it is hard to reconcile this with Loeb's apparently well-founded statement that collagen can combine only with bases on the alkaline side of the isoelectric point. The chrome salts exist commonly in two different states, a green and a purple one, but little is known about the cause of the color change and both green and purple salts seem to be able to tan.

On the whole, it seems, therefore, that we must admit that we have no single theory which will account for all the various phenomena which we class as tannage, and it is safest to suppose that the hide fiber can be converted into substances which we must call "leather" in several different ways, which often cooperate in producing the commercial article. We may instance the following at least:

1. By mere dehydration of the separated fibrils in such a way that they can be dried without adhesion.
2. By actual changes in the chemical nature of the fibrils, which destroy their adhesive character.

<sup>9</sup> *Collegium*, **11** (1912), 54, 420.

<sup>10</sup> Le tannage au brome, *Collegium*, **10** (1911), 289, 373.



3. By coating the fibers with fine powders or precipitates, or, perhaps, fatty matters, which mechanically separate them.

This summary does not attempt to deal with the chemical and mechanical means by which these changes are caused, and which have been already discussed at some length in the preceding pages.

## CHAPTER XXXI

### GELATIN AND GLUE

By

ROBERT HERMAN BOGUE

Gelatin, together with its less aesthetic sister, glue, bears the unique distinction of being the original colloid, or type substance of the class. And not only to Graham, but to the great majority of those who have followed him, gelatin has furnished the material upon which experimentation of the colloidal state has been largely conducted.

Any exhaustive exposition of the *colloid chemistry* of these substances would include a consideration of:

The raw skin

The conversion of raw stock to gelatin or glue

The colloidal behavior of the material

The structure of gelatin in its several states

The economic and industrial uses which are dependent upon the colloidal state of the substance.

Much of this material, however, has received very specific treatment in other chapters of this treatise. Thus, the raw skin is discussed in Chap. XXX by Procter; the colloidal behavior of gelatin is discussed in Chap. II by Loeb; the structure is discussed in Chap. XV by Weiser; and some of the uses dependent upon the colloidal state in Chap. XXIX by McCollum. In order that duplication may be avoided, these topics will not be reconsidered at this place, but attention will be concentrated on the conversion of the raw stock to gelatin, with particular emphasis upon those processes which are controlled by a direct application of the principles governing the colloid state.

There is little in the chemistry or technology of the gelatin and glue industry which is not distinctly and specifically a colloid-chemical or colloid-physical process. The raw stock, *i.e.*, the collagen, from which gelatin is derived by hydrolysis, as well as

the ultimate product, gelatin, admixed with numerous impurities of other proteins, soaps, fatty material, etc., is at all times in the colloidal state, and usually several manifestations of colloid phenomena are coexistent in the same material. These will be given consideration as they occur in the process of conversion of collagen to gelatin.

### MANUFACTURING PROCESSES

**Raw Materials.**—The raw materials for the manufacture of gelatin and glue may consist, generally, of all parts of the body of the ox, calf, sheep, or other animal wherein collagen is the chief constituent. The white middle portion of the skin, called the corium, is nearly pure collagen. The sinews, tendons, and other white connective tissues are rich in collagen. The organic matrix of the bones consists largely of this parent protein of gelatin. Other tissues contain smaller amounts of collagen, but not in sufficient quantity to make extraction practicable.

Of the materials mentioned, the skin is the most important raw material. Nearly all of this, however, goes to the tanner, and only the trimmings, the fleshings, and the skivings find their way to the glue manufacturer. Sinews and bones of all kinds are used. The latter may be degreased with organic solvents and the mineral material largely removed with acids before hydrolysis. The product of these two operations is called *ossein* and is employed principally for the manufacture of edible gelatin.

**Preparation and Preservation of the Stock.**—Many glue houses are located within easy reach of the packing houses and tanneries in the large cities, and much of this stock is made up into glue at once. But, on the other hand, large amounts of stock are shipped long distances, as from South America, and require a special treatment before shipment to prevent bacterial and maggot decomposition.

Salt, lime, and desiccation are commonly used. The salt treatment is preferred in this country. It consists in piling the stock in alternate layers with salt. The skin pieces then behave as semi-permeable membranes enclosing a watery solution. Some of the salt dissolves, forming a concentrated salt solution, and by osmosis the water within the skins passes through the membranes, tending to dilute the salt solution. This water is

allowed to drain off, and a sufficient amount of salt is present so that the drying out and shrinking of the hide pieces may continue until a hard, dry product results. This will keep almost indefinitely.

The lime treatment consists in piling the stock with an excess of lime paste. There results with time, however, an inevitable loss due to hydrolysis, for the lime acts chemically on the collagen, due to its content of hydroxyl ions, breaking down the complex protein to gelatin and even more degraded forms, as proteoses, peptones, and amino acids. Long storage with lime, therefore, must be avoided if serious losses are to be prevented. Short periods of storage, on the other hand, are favored by the lime treatment, for the subsequent liming operation preparatory to cooking may by such practice be shortened. The hide becomes somewhat swollen and is in a better condition for the initiation of the glue-making process than when treated by other means.

Complete desiccation of the raw stock sometimes is used, but a hard product results which yields to the subsequent liming and cooking processes with distressing slowness.

**Soaking and Washing.**—Whether the stock is in the fresh or in the salted condition, the first treatment is always a thorough washing with water. This removes the blood and dirt, which are always present in fresh stock, and the salt and dirt from salted stock. If blood is allowed to remain in the stock when the extractions are made, the glue will be turbid and muddy in appearance. In salted stock there is always a considerable amount of dirt present. In Chap. II it was shown that salts, in general, depress the swelling of gelatin, and the same is true with respect to the action of salts on collagen. For this reason it is important that the salt used as a preservative be washed out completely before treatment with lime.

**Liming.**—After washing, the hide stock is allowed to stand in vats with a suspension of lime in water. The stock is put into fresh vats of lime suspension every two or three weeks for a period of from six to twelve weeks.

The most obvious changes that are induced by the liming operation are the greatly increased volume and the loosening of the hair. The hide pieces increase to several times their original cross-section, and take on a firm, rigid appearance. If



the hair has not actually fallen off during the lime treatment, it will be found to be held so loosely that a gentle rubbing with the fingers will suffice to remove it. Procter believes the bacteria present are responsible for this latter action.

Perhaps less obvious, but of more importance, are the chemical changes involved. If raw hide pieces were heated with water, solution would be effected very slowly unless a temperature above  $100^{\circ}$  (under pressure) were used. But gelatin is a heat-sensitive substance, and, when exposed to high temperatures, rapidly undergoes a decomposition, breaking up into constituents which have very little or no value as jelly producers or adhesives. As a result of the lime treatment, however, the hide pieces are enabled to pass into solution by only a moderate heat treatment with water, and the valuable properties of the gelatin are preserved.

The plumping action appears to be due to a particular concentration of hydroxyl ions. (The mechanical and theoretical conditions governing this action are described fully in the chapters by Procter and by Wilson.) If portions of a neutral hide are immersed in water containing increasing amounts of alkali or of acid, the hide swells more as larger amounts of alkali or acid are added (there is at first a slight decrease in volume on adding acid) until a certain maximum of swelling is attained, and, if still more alkali or acid is added beyond this point, the swelling becomes less and solution takes place. The alkalinity of a saturated solution of lime is very close to that alkalinity at which maximum swelling occurs.

But if only a saturated solution of lime in water is added and the alkalinity of the solution is tested at regular intervals after introducing the hide pieces, it is found very rapidly to become less alkaline, and is soon almost neutral. This would also be the case with any other alkaline or acid substance, and is due to the ability of the hide to react with hydroxyl or hydrogen ions, respectively. By using a suspension of the lime in water, this difficulty is overcome, for, as rapidly as the hydroxyl ions are removed by the hide, just so rapidly will the undissolved lime pass into solution. By this means the alkalinity of the mixture is automatically held constant. It is this property of a nearly foolproof and auto-

matically controlled alkalinity that makes lime better than most other reagents for this service.

Besides collagen, which is converted into gelatin by heating in water, glue stock contains several other proteins that have no value whatsoever in glue. Elastin is found in the connective tissue, mucin is found in cartilage, keratin is contained in hair, and albumins are always present. If these substances were allowed to be cooked with the stock, the product would be weakened and would also give a glue that was turbid, muddy, or opaque. These proteins, especially the albumin and mucin, are soluble in alkaline solutions, and so are dissolved out of the stock by the lime. Here again the lime is particularly well adapted for the purpose, as solutions of stronger alkalinity would dissolve also increasing amounts of the collagen, and solutions of weaker alkalinity would not be effective in dissolving even the albumins or mucins.

As the albumins and elastin are attacked by the lime, the roots of the hair become loosened, for they are embedded directly in the layer of elastin below the epidermis. The hair, having no longer any support, falls out or is easily rubbed off. Some of the fat of the stock is also acted upon by the lime, forming insoluble lime soaps which should be removed in the washing process if a clear product is desired.

Lime itself is a very good germicide for most microbiological organisms. There are some forms of bacteria which thrive in lime solutions and high counts have been obtained of these, but the putrefactive organisms are almost entirely killed or inhibited. In general, it is quite unnecessary to add other preservatives during the liming process.

It is important to use care in the selection of the lime for hide swelling, for it has been found that dolomitic limes which contain large amounts of magnesia are decidedly inferior to the high calcium limes. For some reason which is not entirely clear, the magnesia tends to offset the normal swelling induced by the lime. In practice, it is usually most satisfactory to procure a high-grade quicklime and slake it at the plant just prior to use.

The iron oxide content of the lime should likewise be low, as otherwise the color imparted by it to the finished glue or gelatin may be objectionable, and bleaching may then be necessary.

**Washing and Deliming.**—The liming operation is allowed to continue until the inner portions have been practically cleared of their mucins and the stock shows a uniform and firm plump condition. It is then necessary to remove completely the lime and the products which have been brought into solution. Pure water is used first, and this is followed by adding a dilute solution of some acid to neutralize the last traces of lime and, generally, to impart a slight acidity to the stock prior to hydrolysis.

The maximum swelling of gelatin occurs at a pH of about 3.6, but, as will be shown later, it is impracticable in the plant to obtain this degree of acidity. Calcium or magnesium salts seriously interfere with swelling, and must, accordingly, be washed out completely.

The acids commonly used are sulfurous, hydrochloric, and phosphoric acids. Sulfurous acid, besides producing excellent swelling, has both bleaching and antiseptic action, and so is preferred in glue manufacture, but is prohibited except in very small amounts in edible gelatin. Hydrochloric acid often contains arsenic and, therefore, phosphoric acid is most generally used in the manufacture of food gelatin.

**The Hydrolysis.**—The “boiling process,” as this is commonly called, is the process with which we are most concerned in glue manufacture, first, because it is the most vital part of the process, and, second, because it has most to do with colloid chemical control.

The primitive method of cooking glue consisted in heating the stock with a large quantity of water over an open fire until practically all the stock had gone into solution. The time necessary to hydrolyze the last portions was so great that much of the earlier hydrolyzed gelatin was changed into more degraded forms, and much of its value thereby lost.

The modern methods of extraction make attempt, by one means or another, to avoid an excessive hydrolysis of the gelatin first extracted, while at the same time obtaining complete extraction of the more refractory material. This is commonly brought about by making five or six separate extractions. The temperature of the first will be about 70° for a period of about six hours. The temperature is brought higher for each extraction until at the last it is boiled or even treated in autoclaves under pres-

sure. The time of each extraction is also increased. Various forms of continuous extractors have been introduced, but their adoption is not general.

The fat which collects during the first extraction is skimmed off by hand, or allowed to run off from the surface. This forms a valuable by-product of the industry.

At the close of each extraction the gelatin, which has gone into a colloidal solution in the water, is drained off through a coarse filter of excelsior, placed beneath the false bottom of the vat, into storage tanks for further treatment. The first extractions from a large number of vats are brought together, and these are known throughout the rest of the process as the "first run." The other extractions are treated similarly. Frequently, two consecutive "runs" will be combined, depending on the demand for a particular quality of product.

From a study of the properties of the different glues resulting from a very large number of water changes, Shuey<sup>1</sup> has shown that "the first glue to be dissolved is that which was so highly hydrolyzed in liming that raising the temperature is all that is needed to bring it into solution." There is no time element involved in this case, for a portion of the stock is already converted to gelatin, and so goes at once into solution.

There are so many factors entering into the hydrolysis of the collagen to gelatin, and of gelatin to its cleavage products, that, in order to understand adequately the function of each of these, it is necessary to make a systematic study wherein each in turn is caused to vary while all others are held constant. As a result of such a study, Bogue<sup>2</sup> has demonstrated the particular function and curve of usefulness surrounding the following variable conditions:

- Hydrogen ion concentration ,
- Presence of salts
- Temperature
- Duration of heating
- Ratio of stock to water

<sup>1</sup> See BOGUE, R. H.: "Chemistry and Technology of Gelatin and Glue," New York, 1922, p. 285.

<sup>2</sup> *Ind. Eng. Chem.*, **15** (1923), 1154; Colloid Symposium Monograph, Univ. of Wisconsin, 1923, p. 265.



Agitation

Condition of stock

The plumping reagent

The procedure involved an hydrolysis in water or other electrolyte for a definite period at a definite temperature. The distribution of the nitrogen between that recovered in the solution, that evolved as ammonia during hydrolysis, and that remaining in the residue was determined. The amino nitrogen of the solu-

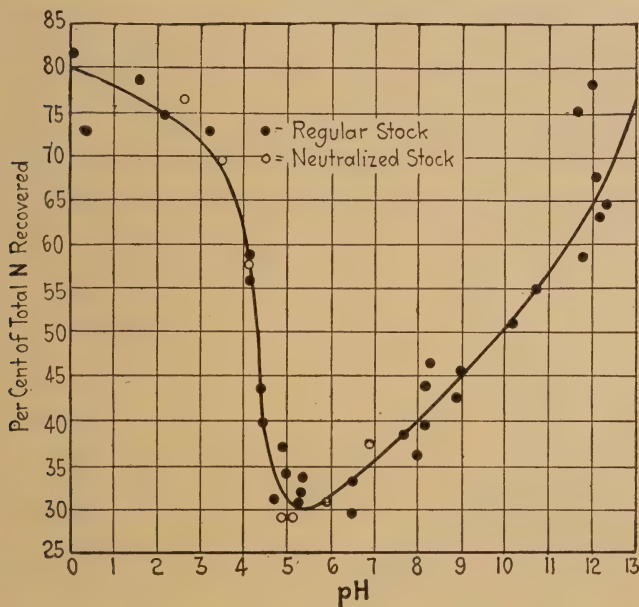


FIG. 1.—Effect of  $H^+$  ion concentration of hydrolyzing solution on the percentage of the total nitrogen recovered in the solution.

tion, the  $H^+$  ion concentration, the viscosity, and the jelly consistency also were determined.

Some of the data obtained are shown in Figs. 1 and 2. The rate of hydrolysis obviously is least at a pH of 5 to 6, but, on increasing the acidity to pH 3 to 4, the hydrolysis becomes very rapid. Increasing concentrations of alkali also increase the hydrolysis, but less rapidly. The secondary hydrolysis, which involves the breakdown of the gelatin molecule to proteoses, peptones, and amino acids, is indicated in Fig. 2. Throughout the range of

pH 3 to 8 this breakdown is not excessive, but beyond either of these limits it becomes high. The period of heating in these cases was 8 hours, and the temperature 80°. Longer periods or higher temperatures very considerably increased the rate of both the primary and the secondary hydrolysis, but the general shape of the curves remains the same. At high temperatures, however (95°), and at long periods of heating (168 hours) the curves flatten out. That is, the specific influence of  $H^+$  ion

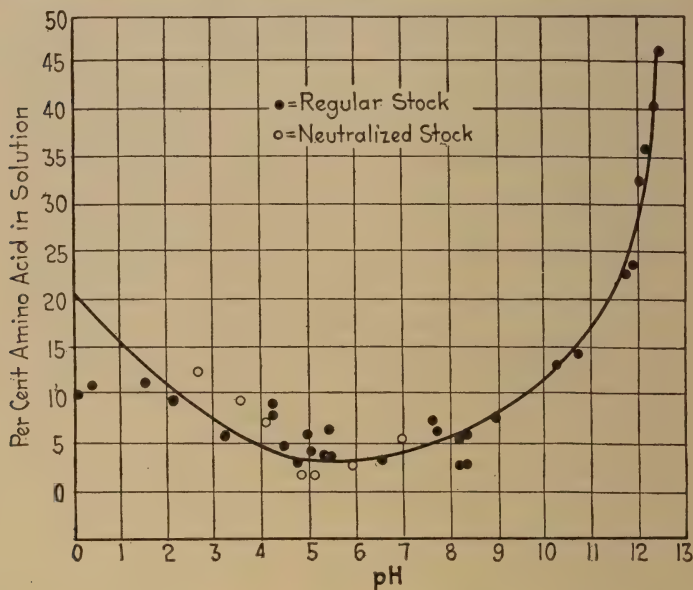


FIG. 2.—Effect of  $H^+$  ion concentration of hydrolyzing solution on the percentage of amino-acid nitrogen recovered in the solution.

concentration becomes of but little importance. The loss of nitrogen as ammonia becomes important at high concentrations of alkali, especially when the period of heating is prolonged.

The viscosity and jelly consistency show distinct minima at pH 4.5 to 5.0 and maxima at pH 7.5 to 8.0. Increases in the ratio of water to stock hastened somewhat the hydrolysis of collagen to gelatin, but seemed to be practically without influence on the secondary hydrolysis of gelatin to its degradation products. The ratio of 12 parts of water to 1 part of dry stock was found

to be optimum. A rapid agitation was found to hasten the primary hydrolysis, but to be without influence on the secondary hydrolysis. Finely cut stock was converted to gelatin more rapidly than the coarsely cut material, but the gelatin produced was somewhat more degraded at the end of the operation, due to the longer exposure to the hydrolyzing conditions. The previous treatment of the stock was found to influence greatly the nature of the product. Lime-treated stock gave a high yield of gelatin, which was only moderately degraded into proteoses, etc. The least secondary hydrolysis occurred in stock plumped with lactic acid; the highest viscosity and jelly strength, in stock plumped with borax. The alkaline reagents gave a hide that was firm and plump and went easily into solution, but the excessive hydrolysis into amino acids was more pronounced than in the acid-swollen stock. The latter was limp but gave a product of high viscosity and jelly strength.

**Clarification and Filtration.**—The liquid which runs from the boiling vats contains much material in suspension, which must be removed if a clear product is to result. This matter consists of unhydrolyzed portions of hide, bone, or hair, or of insoluble products, either separated from the stock during hydrolysis as albumins, mucins, grease, or mineral salts, or produced during the hydrolysis, as lime soaps.

The processes which suggest themselves for removing this suspended matter are: (1) gravity settling; (2) centrifugal separation, (3) filtration; (4) adsorption; (5) precipitation; and (6) coagulation; or a combination of two or more of these.

Gravity; settling will effect the separation only of the largest and heaviest particles, unless continued for an excessively long period, because of the high viscosity of the glue liquors. At best, this will remove only a small part of the material responsible for turbidity. Centrifugal separation has been applied in many plants, but has met with only mediocre success. The heavier particles are readily removed by this process, but unless the liquors are very dilute, the capacity per machine is low. And, of more importance, centrifuging fails to remove the protein impurities, as the albumins and mucins, and the lime soaps. These are probably hydrated and emulsified in the glue liquors, and, moreover, have nearly the same density as the gelatin itself.

Filtration through presses has been used extensively, but the operation of presses is difficult and uncertain. The densely packed filter medium quickly becomes clogged by the slimy mucins and soaps and, if the temperature is not maintained sufficiently high, the gelatin itself will congeal in the pores. The presses require very frequent changing, therefore, to prevent blocking and breaking through.

A study of glue filtration has shown that far better results are secured when the filtering medium has a very great surface exposure, and this is true nearly irrespective of the size of the apertures. This places the filtering problem in the field of adsorption. Gelatin itself in neutral solution is slightly negative in an electric field. The mucins and albumins also are negative, but are hydrated to a very much less degree than the gelatin. In the presence of a positively charged substance, these impurities accordingly adhere to it, lose their charge either by physical neutralization or chemical combination, and may be thereby separated from the containing liquid. The filtration of water and of sewage makes use of this same principle.<sup>3</sup> The conditions necessary, therefore, in the filtration of glue or gelatin solutions are, first, a filtering medium positive with respect to mucins, albumins, etc.; second, an enormous surface exposure; and, third, only moderate pressure and relatively loose packing. In practice the most successful filter medium used at present is cellulose, the form being a good grade of cotton paper pulp. This is slightly acidic (negatively charged), but is positive to the mucins and albumins. Charcoal gives good results but is more quickly clogged than the cellulose, as it is more positive. Fuller's earth, which is strongly negative, improves the liquor hardly at all, while alumina, which is strongly positive, adsorbs the gelatin as well as the other proteins, and the filter clogs almost immediately.

The glue liquors, obtained by filtration, are perfectly clear but upon concentration, which must take place before gelation, a slight opacity frequently results. This is due largely to the presence of difficultly soluble inorganic salts which are present in nearly saturated solution, and which tend to separate out upon further concentration. The gelatin acts as a protective colloid

<sup>3</sup> See Chap. XXXIV on Sanitation.



in preventing precipitation of large crystals, but a considerable number of small nuclei appear, which rob the product of its brilliancy. They consist largely of salts of calcium and may be partially removed by precipitation. Sulfurous acid will precipitate out calcium sulfite and any excess may be removed, if desired, by heat or by an oxidizing agent as hydrogen peroxide. Phosphoric acid is sometimes used, and alum and lime may be caused to combine in the liquors to produce aluminium hydroxide and calcium sulfate. These precipitates are in all cases filtered off, or the liquors allowed to stand and then syphoned off from the sediment.

A much more sparkling product is obtained by bringing about a coagulation in the liquor with egg albumin or blood albumin. A water solution of the albumin is added to the comparatively cool glue liquor, and the temperature then slowly raised until the albumin coagulates. The mixture is allowed to stand until the coagulation has settled and then the clear liquor syphoned off and filtered. This gives a remarkably brilliant product, but it has suffered somewhat in quality, due to the prolonged high temperature of coagulation, and the process is decidedly more expensive than any of the others. For removing salts which are objectionable in photographic gelatin, such as chlorides, a further treatment with silver salts is sometimes applied.

A study of the control of salt content throughout the process from the hydrolysis to the gelation has been made by Shuey.<sup>4</sup> He shows, by conductivity methods, the variation in salt content resulting at each step in the process. The greatest lowering in conductivity is shown to follow the addition of a precipitant.

**Evaporation.**—The higher grades of gelatin will produce a jelly on cooling at a concentration of 5 per cent, but for the more highly hydrolyzed products a higher concentration is required. Since the usual methods for finishing a glue or gelatin involve the drying out of the jelly, it becomes necessary that the liquors be concentrated to such a degree that a firm jelly will result on chilling. This degree will vary from 5 to 30 per cent in concentration, and in many cases is continued to a concentration of 50 per cent.

<sup>4</sup> See BOGUE, R. H.: "Chemistry and Technology of Gelatin and Glue," New York, 1922, p. 289.

Evaporation by boiling in an open kettle is obviously not permissible because it would bring about excessive hydrolysis of the gelatin to more degraded forms. This hydrolysis has been shown<sup>5</sup> to be proportional directly to the temperature and to the duration of heating (at any given pH, etc.). For this reason, the lowest possible temperature and the briefest period of heating should be employed. Many forms of double-effect vacuum evaporators are in use. The greatest economy of grade is secured by passing the liquors first through the high-temperature, low-vacuum side, and, after a preliminary concentration here, into the low-temperature, high-vacuum compartment. Some loss inevitably will be experienced, but, by maintaining the highest vacuum consistent with rapid evaporation, this will not be serious. The evaporator should be constructed so as to give a high surface area for the evaporation, so that only a small volume of glue liquor need be present at one time. This will reduce the time factor. Some glue liquors foam excessively, and a large space should be provided for breaking this up. The proteoses, soaps, and alkalies are especially prominent causes of foam.

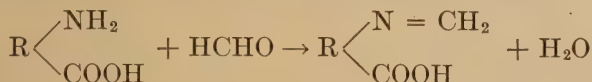
If the glue or gelatin is to be made into a special product, the required material is added at this time. For example, if a flexible glue, such as is employed for printers' rollers or hectograph plates, is wanted, sugar, glycerin, and other ingredients may be added. If to be used in calsomine, zinc oxide, lead carbonate, or calcium carbonate may be ground in. Preservatives may be added at this point, but, except when indispensable to prevent putrefaction, they should be avoided.

In practice, it is observed that nearly all preservatives tend to decrease the jelly consistency of the product, and that they usually also affect the viscosity, in some cases raising and in other cases lowering it. This is probably due to the influence of the added substance on the degree of dispersion of the colloid, or on its ability to combine chemically with the gelatin molecules. Formaldehyde, for example, produces an enormous increase in viscosity, which very quickly imparts to the glue liquor the consistency of warm, stringy rubber. A high temperature and a high concentration both favor the formation of this rubber-like jelly. It cannot be brought into solution again, as the reaction

<sup>5</sup> BOGUE, R. H.: *Chem. Met. Eng.*, **23** (1920), 201.

is entirely irreversible. The jelly consistency, however, has decreased, although a hard, horny layer quickly forms on the surface.

Formaldehyde has been shown<sup>6</sup> to react chemically with proteins, or any compound containing the amino acid structure, combining with the amino group and forming a neutral methylene imino group. This is represented by the reaction:



The product apparently polymerizes with the formation of an insoluble but highly cohesive jelly. This polymerization effects an enormous increase in viscosity (or plasticity), but the decreased ability of the gelatin molecules to hold water of hydration produces, it seems, a decrease in jelly consistency. Thus, the viscosity is again shown to be dependent on the chemical reactivity of the gelatin,<sup>7</sup> and this is shown to affect the hydration and particle size.

While the reactions with other antiseptics may be less obvious than with formaldehyde, it is probably true that in many cases the hydration and particle size are affected. This in some cases is revealed by peptization; in other cases, by coagulation. It is probable that the same forces which affect the gelatin may also be responsible for the solution or the agglutination of the bacteria, when this is effected.

**Drying.**—The liquors now have to be dried for shipment, except such as have been especially treated to prevent gelation. The common practice is to allow the liquors to chill to a jelly, and to spread this jelly on nets in an air tunnel, where it remains until dry.

The old method, which is still used a great deal, is as follows: The concentrated liquors are run into pans of galvanized iron and these are set in chill rooms until a stiff jelly is formed. The block of jelly is loosened by placing in steam or hot water for a moment, and is cut into slabs by piano wire or knives. These slabs are placed on nets of wire or cotton and the nets stacked in

<sup>6</sup> See SÖRENSEN: *Biochem. Z.*, **7** (1908), 45.

<sup>7</sup> See LOEB, J.: "Proteins and the Theory of Colloidal Behavior," New York, 1922, p. 195; Cf. also this book, Chap. II, p. 61.

the drying alleys. The process is very sloppy and laborious. The chill rooms are not easily kept in a sanitary condition, and molds and bacteria develop rapidly in the jellies. The cutting entails the discard of much jelly and this must be remelted and rechilled to be cut again.

A form of machine developed by Kind and Landesmann<sup>8</sup> marks a decided advance, and is now very generally employed. The liquors are run from a supply tank onto an endless belt of a rubber fabric about a yard wide. This passes slowly through a large chamber cooled by coils of brine from a refrigeration machine. The air is kept in circulation by fans. After about 15 minutes the product, cooled to a stiff jelly, emerges on the belt. It is taken off automatically onto frames and these are stacked as before in the drying alleys. The process has the advantage of being continuous and very rapid compared with the old method. There is no waste or remelting necessary, and the possibility of bacterial or mold contamination is remote.

Two methods of direct drying without passing through the jelly stage or the drying alleys have been used. One of these, sometimes spoken of as the roller-drying process, is used only with low-grade glues and to meet a demand for a cold-water-soluble product. The glue liquor is placed in a pan beneath a large steel drum revolving slowly. The drum is heated with live steam inside, and, as the liquors adhere to the drum as it revolves, they are dried to a powder by the time it has completed the revolution. The powder is scraped off by a knife just before it dips again into the liquors. The product containing a large percentage of proteoses and peptones is hygroscopic, and in hot and humid weather often takes up sufficient water to melt the material and much loss results. It finds a special use for incorporation into rubber, where water is particularly undesirable, and for cold-water calsomine.

Spray drying has not been generally adopted, but the advantages of the process are so great that it is inevitable that this method will become of industrial importance in the near future. The chief obstacles to adoption have been the high cost of installation, the uncertainty attendant upon a new process, and the necessity of educating the consumer to a differently appearing

<sup>8</sup> U. S. Patent 1046307 (1912).



product. With the experimental stage satisfactorily passed, there should be no longer any hesitancy on the part of the manufacturer to install the necessary equipment. This would eliminate at a stroke (1) the concentration process by evaporation in vacuo; (2) the chilling; (3) the spreading on trays; (4) the drying in the alleys; and (5) the grinding. In fact, the entire operation, taking the liquors at once after passing through the filters, is performed by passing them through the spray-drying machine. The liquors are forced out of a fine nozzle under pressure into a warmed area of diminished pressure, and the fine droplets almost immediately lose their content of water and all as fine, hollow, spherical particles of white dust. Where tests have been made, it appears that the grade does not suffer at all, but is rather higher than would result from the usual treatment. The fineness of the product makes it possible to put it into solution at once, stirring into cold water and heating immediately. The saving resulting from reducing the labor, the extensive equipment, the floor space and chill rooms, the time, and the spoilage from bacteria and high humidity in summer would be impressive.

All glues which have been chilled and spread onto trays are dried out in tunnels or alleys. These are constructed so as to receive trucks stacked with frames of the jelly. The trucks enter at one end of the alley and are withdrawn at the other end. Heated air is blown through in a direction countercurrent to the progress of the trucks. This subjects the fresh jelly to a flow of air nearly saturated with water vapor, while the nearly dried glue meets the driest air. This is important for the prevention of case-hardening, for if dry air came in contact with the fresh jelly, a thin film of dry glue would be formed on the surface and this would greatly hinder and retard the proper drying out of the inner portions of the jelly.

The successful operation of the drying alleys depends upon the care exercised in regulating the temperature of the incoming air to as high a value as possible without melting the jelly, for air at a high temperature is capable of holding, at saturation, a considerably greater quantity of water than at a lower temperature. By noting the wet bulb temperature, as well as the actual temperature, it is observed at once to what temperature the air will be cooled by becoming saturated with water vapor. If the

alleys are sufficiently long, and fresh stacks are placed at the air outlet end, the air will be saturated as it leaves the alley, and the temperature consequently reduced as calculated. This latter temperature should be only slightly below the melting point of the fresh jelly. The higher temperature at the inlet end will do no damage, as the jelly is there nearly dry, while the drying efficiency of the air so heated is vastly increased.

**Finishing.**—When the glue or gelatin has been dried to a condition of equilibrium with the air, it will still retain a water content (removable by heating to 110°) of 10 to 18 per cent. Occasional samples may run beyond these limits. In general, the lower grades retain a smaller amount of water, and this accounts, in part, for their lower adhesive value. The writer<sup>9</sup> has found that low-grade glues which were reduced in water content, by being placed in a dry atmosphere, to 11.5 per cent could no longer even retain their shape, but crumbled to bits, while at a water content of 15 per cent the same glues possessed considerable tensile strength. A high gelatin content was found in all cases to be coincident with a greater hygroscopicity, while those glues which contained most of their nitrogen as proteose or peptone retained but little water and were weak in adhesive value. The water-holding capacity of a glue is thus shown to be dependent on the gelatin content, and this, in turn, to determine, perhaps by virtue, in part, of the water which it will retain at equilibrium with the air, the adhesive value of the glue.

The form of the finished glue is determined largely by the demands of the market. Sheet, ribbon, and noodle glues are produced by the old method of pan chilling, wire cutting, and hand spreading. The glue is about a  $\frac{1}{4}$  in. thick and requires long soaking before it can be brought into solution. Due to the shrinking effect in drying, as shown by Sheppard,<sup>10</sup> the edges will be much thicker than the center portion, and, unless the utmost care is exercised, case-hardening is certain to follow. Any salts present in excess will separate out in the more concentrated area in the center of the sheet and give it an opaque appearance.

<sup>9</sup> BOGUE, R. H.: "Chemistry and Technology of Gelatin and Glue," New York, 1922, p. 422.

<sup>10</sup> SHEPPARD, S. E.: *J. Am. Chem. Soc.*, **44** (1922), 373.

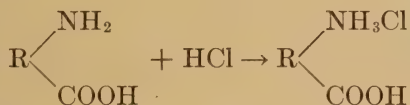
Flake glue is the product of the continuous-belt machines and has been passed through a crusher of the hammer mill or disintegrator type. Ground glue is further passed through a rotary fine crusher, and for some special purposes it may be ground to still finer size or to a powder.

#### SCIENTIFIC CONTROL IN MANUFACTURE

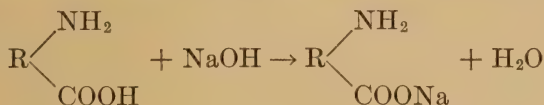
**The Amphoteric Behavior of Gelatin.**—Loeb<sup>11</sup> has demonstrated that gelatin combines with the anion of acids or of salts when the hydrogen ion concentration is greater (the pH less) than pH 4.7, and with the cation of bases or of salts when the hydrogen ion concentration is less (the pH greater) than pH 4.7. If this is so, and there is an increasing volume of evidence in support of the contention, then isoelectric gelatin may be

regarded simply as  $R \begin{matrix} \nearrow NH_2 \\ \searrow COOH \end{matrix}$ . The isoelectric gelatin was

found by Loeb to be inactive to either anion or cation of added salts. The addition of an acid (*i.e.*, hydrochloric) would result in the reaction



producing gelatin chloride in this case. The addition of a base (*i.e.*, sodium hydroxide) would result in the reaction

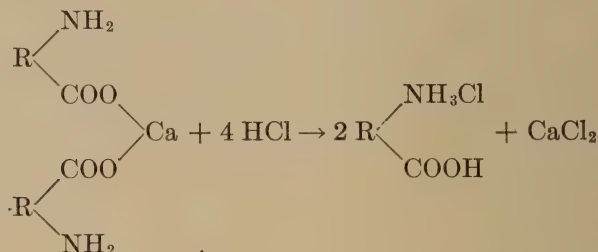


forming sodium gelatinate. J. A. Wilson<sup>12</sup> has shown that gelatin behaves as a monacid base in its action towards acids, and has found it to have a limiting equivalency of 768 g. of gelatin to 1 mol of hydrochloric acid. This value may, therefore, be assigned as the combining weight or equivalent weight of gelatin.

<sup>11</sup> Cf. Chap. II.

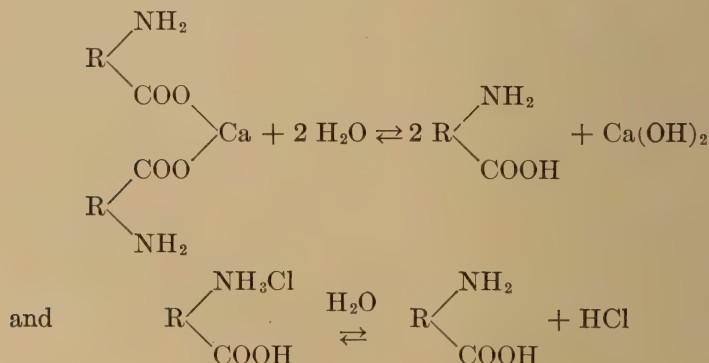
<sup>12</sup> Cf. Chap. I.

Ordinary gelatin has a pH value of nearly 7.0 and is found to consist largely of calcium gelatinate, since lime is used in the manufacture. If hydrochloric acid is added in such quantity as to neutralize the lime and also combine with the gelatin, we could write



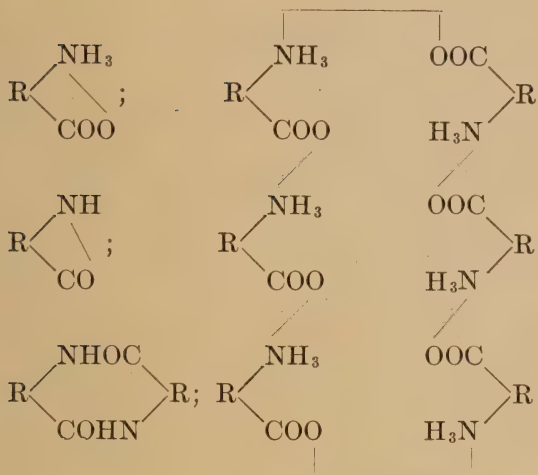
This assumes, of course, the complete conversion of calcium gelatinate to gelatin chloride.

A principle in physical chemistry requires that a salt consisting of an anion or cation, which by action with water may produce a less highly ionized acid or base, will hydrolyze in the presence of water. Both the gelatin salts and the metal gelatinates satisfy this condition, for both of these are ionized to a far greater extent than the isoelectric product, as proved by Loeb. We would, therefore, expect hydrolysis such as represented by the following reactions:



And the isoelectric gelatin itself would doubtless form internally neutralized molecules and polymerized molecules, such as





Evidence for some such polymerization is found in the cloudy, almost milky, appearance of a solution of isoelectric gelatin; the ready visibility of submicrons under the ultramicroscope; the failure of the material to become highly hydrated; the low osmotic pressure; and the non-conductivity of the material for the electric current.

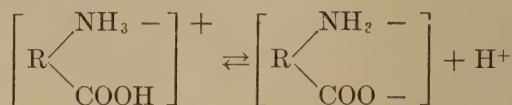
Upon examining the formulas given above, it will be obvious that gelatin chloride, for example, can ionize, giving the gelatin

cation  $\left[ \begin{array}{c} \text{NH}_3 - \\ \diagup \quad \diagdown \\ \text{R} \quad \quad \text{COOH} \end{array} \right]^+$  and the anion  $\text{Cl}^-$ ; also that the sodium

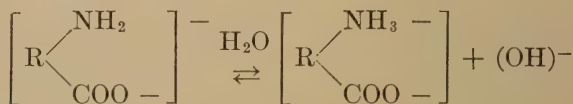
gelatinate can ionize, giving the gelatin anion  $\left[ \begin{array}{c} \text{NH}_2 \\ \diagup \quad \diagdown \\ \text{R} \quad \quad \text{COO} - \end{array} \right]^-$

and the cation  $\text{Na}^+$ . But, as the hydrolysis is decidedly marked in both cases, it will be necessary to have present an excess of hydrogen ions to prevent hydrolysis of the gelatin salt, and an excess of hydroxyl ions to prevent hydrolysis of the gelatinate. These salts cannot, therefore, be obtained in solution in pure form except in the presence of excess  $\text{H}^+$  or  $(\text{OH})^-$  ions respectively.

These reactions show also why gelatin cation, for example, can combine only with the anions of added salts. The acid ionization of the gelatin cation



is quite suppressed by the excess of  $\text{H}^+$  ions which must be present. But if these  $\text{H}^+$  ions are removed, as by the presence of a base, then this reaction will proceed, and if sufficient  $(\text{OH})^-$  be present to pass beyond the isoelectric point, the gelatin will, of course, react with cations. In a similar manner, the basic ionization of the gelatin anion



would be quite suppressed in the presence of excess of a base, so combination of the ion with anions would be impossible.

The reactive part of the gelatin molecule in its behavior towards inorganic ions is not confined to terminal  $-\text{NH}_2$  and  $-\text{COOH}$  groups, as has been shown repeatedly,<sup>13</sup> but is found also in the internal  $-\text{COHN}-$  groups. This group may exist

in the keto form,  $\text{R} - \overset{\text{H}}{\underset{|}{\text{N}}} - \overset{\text{O}}{\parallel} \text{C} - \text{R}$  or the enol form

$\text{R} - \text{N} = \overset{\text{OH}}{\underset{|}{\text{C}}} - \text{R}$ . With acids, as hydrochloric, the reaction

would produce  $\text{R} - \overset{\text{H}}{\diagdown} \overset{\text{Cl}}{\underset{|}{\text{N}}} = \overset{\text{OH}}{\underset{|}{\text{C}}} - \text{R}$ , and with bases, as sodium hydroxide,  $\text{R} - \text{N} = \overset{\text{ONa}}{\underset{|}{\text{C}}} - \text{R}$ , if we assume that the enol form is the one

primarily responsible for these reactions. There is probably an equilibrium between the two forms, but, as either reaction

<sup>13</sup> Cf. BOGUE: "Chemistry and Technology of Gelatin and Glue," McGraw-Hill Book Co., 1922, Chap. V.

proceeds, the keto form gives place to the enol form. However, as far as the equivalence of the gelatin is concerned, the internal reactive groups behave in the same manner as the terminal groups and need not be considered separately.

**Isoelectric Gelatin.**—From these considerations it will be obvious that the only pure gelatin will be isoelectric, since it may be neither an anion nor a cation of a compound; it will contain no ash, since all inorganic material will be absent; and it will contain no hydrolytic products. Ash-free isoelectric gelatin was prepared by Loeb<sup>14</sup> and Miss Field<sup>15</sup> by allowing hydrochloric acid of the proper concentration—which varied from  $N/128$  to  $N/512$ , depending on the nature of the stock gelatin—to react with the granulated gelatin for a half hour at  $10^{\circ}$  and then washing out the excess of acid as thoroughly as possible with cold distilled water. The hydrochloric acid reacts with the calcium gelatin-ate, forming calcium chloride, which is washed out, and pure gelatin remains.

C. R. Smith<sup>16</sup> prepared isoelectric gelatin by first washing out the divalent alkali salts with a 10 per cent solution of sodium chloride at  $10^{\circ}$ . The concentration is slowly dropped to 1 per cent and finally distilled water is used until the chlorides are washed out. After this, 90 per cent alcohol is poured over the mass until it has shrunk nearly to dryness, after which it is dried with an electric fan.

S. E. Sheppard and collaborators<sup>17</sup> produce the isoelectric material by carrying out an electrolysis of the gelatin in a large wooden cell. A compartment in the middle is separated from the two outer compartments by filtros, a porous silica septum. The inner cell is filled with a 5 per cent gelatin solution, and distilled water is placed in the two end cells. The anode, placed in one of the outer cells, is of gold, and the cathode, in the opposite outer cell, is of silver. A potential of 110 volts is passed for two weeks, the current dropping during the period from 1 to 0.02 amp. The temperature is kept below  $40^{\circ}$ . The drop in ash content is to about 0.1 per cent. After this treatment, the

<sup>14</sup> *J. Gen. Physiol.*, **1** (1918), 45.

<sup>15</sup> *J. Am. Chem. Soc.*, **43** (1921), 667.

<sup>16</sup> *Ibid.*, **43** (1921), 1350.

<sup>17</sup> *Ibid.*, **44** (1922), 1857.

gelatin is melted at 8 to 10 per cent concentration and precipitated with an equal volume of pure acetone. The gelatin precipitate is removed and the excess acetone distilled off at 70°. Conductivity water is then added to make a 10 per cent solution. This is run out onto a polished nickel or steel chill-table (previously wiped with gasoline to insure stripping), cut into sheets, and dried under uniform conditions on netting. The precipitation further reduces the ash to about 0.03 per cent, and, in addition, removes the greater part of any products of hydrolysis, as proteose, peptone, etc.

For investigational work, it is often imperative that a pure material be used, and for such work the isoelectric gelatin prepared by one of the above methods is available. It is too expensive, however, for an article of general commercial use, and, moreover, is not adapted to general use. The ideal gelatin for most purposes is that one which possesses the maximum of jelly consistency and of viscosity, and gives in a water solution a clear sparkling product. But isoelectric gelatin is found to exist in the condition of minimum viscosity and jelly consistency, and gives a cloudy or milky solution.

The optimum condition for most commercial purposes will be found at the point where the viscosity and jelly consistency are greatest. This is at a pH value of about 3.6. A minimum ash content and a minimum of hydrolysis products are also desirable in the commercial article.

Just how far these optimum conditions can be met in plant practice depends, of course, on the increment of value added to the material by a given operation over and above the added cost involved by that operation. If we regard the combining equivalent of gelatin as 768, as suggested by J. A. Wilson,<sup>18</sup> it should require 36.5 g. of HCl to change 768 g. of isoelectric gelatin to gelatin chloride. It will also require 36.5 g. of HCl to change an equivalent weight of calcium gelatinate to the isoelectric condition. The equivalent weight of calcium gelatinate will be 787; so 73 g. of HCl will convert 787 g. of calcium gelatinate to gelatin chloride (reaction on page 750). On this assumption it will require about 25 lb. of concentrated acid (36 per cent HCl) to each 100 lb. of the stock gelatin.

<sup>18</sup> Cf. Chap. I.



If this acid were added during the cooking process, it would mean the addition of 25 lb. of acid to about 2,000 lb. of water. A more rapid hydrolysis of the collagen would be effected, but a larger portion of the gelatin would also be converted into proteoses and peptones. The loss here and that which would continue in the evaporators would be important. Also the salts present in the gelatin would in no manner be decreased by the addition of acid at this stage of the manufacture.

Another method by which the gelatin chloride might be produced, and which would also decrease the ash content, would be to allow the finished flake gelatin to soak in a cold solution of the acid. The flake would swell and the salts dialyze out, while at the same time the gelatin would combine with the acid, forming, first, isoelectric gelatin, and, finally, gelatin chloride. This would take several days and require frequent changes of water and acid at not over 10°.

In this process, the principle of the Procter-Wilson theory of swelling<sup>19</sup> is the basis of control. The concentration of  $H^+$  ion must be greater outside the jelly than inside and enough must be present in the solution to combine with the calcium gelatinate and to force the reaction to the optimum  $H^+$  ion concentration. Of the two methods suggested, the latter undoubtedly gives the better product, as much of the ash is dialyzed out and no hydrolysis by the acid can take place.

Where this process has been applied directly to plant practice, however, the improvement has been hardly proportional to the added cost of operation.<sup>20</sup> This is easily understood by the following consideration. When a 1 per cent gelatin solution is changed from the point of minimum viscosity (pH 4.7) to that of its maximum value (pH 3.4), the increase in absolute viscosity is found to be about 0.35 centipoise. The increase in a 20 per cent solution would, accordingly, be about 7 centipoises. In the commercial laboratory the pipette or other instrument used for evaluation is sensitive usually to about 5 centipoises, rarely to 1 centipoise. But the difference in viscosity between any two commercial grades, such as the Peter Cooper grades, is from 10 to 20 centipoises. The improvement by a control of  $H^+$

<sup>19</sup> Cf. Chap. I, pp. 10-19.

<sup>20</sup> Cf. BOGUE, R. H.: *J. Phys. Chem.*, **26** (1922), 807.

ion concentration is, therefore, somewhat less than the equivalent of one grade in most instances. As ordinarily determined, the differences between grades represent primarily differences in the products of gelatin hydrolysis in the material.<sup>21</sup>

**The Sol and Gel Forms.**—A conviction that the gel form of such emulsoids as gelatin differed from the sol form in other respects than mere resistance to deformation was established by the early workers in this field. One characteristic after another has been shown to align itself specifically with one or the other of these forms. Intermediate conditions, of course, exist which appear to consist of mixtures of the two forms, but the two forms are probably distinct.

Advance in our knowledge of structure has come largely through the ultramicroscope, but many other evidences are available.<sup>22</sup> By the ultramicroscope McBain<sup>23</sup> has found soap gels to consist of a filamentous structure, and Tarr<sup>24</sup> has observed the same with pectin jellies. Bradford<sup>25</sup> claims to have obtained crystalline gelatin, but Scherrer<sup>26</sup> shows by *x*-ray photographs that gelatin is amorphous. Bogue<sup>27</sup> has described a gelatin sol as consisting of slightly hydrated molecules united into short threads resembling streptococci. The formation of a jelly on cooling involves a lengthening of these threads and an increase in their water-absorbing capacity. When the increased hydration has removed most of the solvent and the adjacent heavily swollen aggregates cohere, a firm jelly is formed. Loeb<sup>28</sup> believes that a gelatin sol contains submicroscopic pieces of solid gelatin occluding water, the relative quantity of which is regulated by the Donnan equilibrium.

C. R. Smith<sup>29</sup> demonstrated that the optical rotation of the sol and the gel forms differed,  $[\alpha]_D$  at 35° and above being  $-140^\circ$ ,

<sup>21</sup> Cf. BOGUE: "Chemistry and Technology of Gelatin and Glue," McGraw-Hill Book Co., 1922, p. 29.

<sup>22</sup> Cf. Chap. XV.

<sup>23</sup> Cf. Chap. XVI.

<sup>24</sup> Cf. Chap. XXVI.

<sup>25</sup> *Biochem. J.*, **14** (1920), 91.

<sup>26</sup> Cf. BOGUE: *Loc. cit.*, p. 144.

<sup>27</sup> *J. Am. Chem. Soc.*, **44** (1922), 1343.

<sup>28</sup> *J. Gen. Physiol.*, **3** (1921), 827; **4** (1921), 73, 97.

<sup>29</sup> *J. Am. Chem. Soc.*, **41** (1919), 135; *J. Ind. Eng. Chem.*, **12** (1920), 878.

and at 15° and below  $[\alpha]_D = -313^\circ$ . He regards 35° as the temperature above which no gel form can exist permanently, and 15° as the temperature below which no sol form is stable.

Davis and Oakes<sup>30</sup> observed a point of minimum viscosity in 1 per cent gelatin solutions at 40° at a pH of 8.0 but none at pH 4.7, the isoelectric point observed by Loeb. Wilson and Gallun<sup>31</sup> reported points of minimum plumping of calf skin at pH 5.1 and 7.6, and later<sup>32</sup> found that gelatin showed a second minimum point of swelling at pH 7.7. They interpret this to indicate that the gel form has an isoelectric point at pH 4.7 but that between pH 4.7 and 7.7 the gel passes into the sol form and that the latter has an isoelectric point at pH 7.7. Both temperature and  $H^+$  ion concentration may be capable, therefore, of transforming the gel to the sol form. Wilson's experiments were carried out at 7°. Mathews<sup>33</sup> has recently added further evidence in support of this critical point, by showing that the absorption spectrum of gelatin has minimum values for the wave length of maximum absorption in the ultra-violet at pH 4.69 and 7.65.

### RETROSPECT

This brief analysis of the applications of colloid chemistry will reveal a multitude of points whereon further investigation would appear to hold promise of fruitful returns. The industry itself is old, indeed one of the most ancient of which we have definite historic record, but the application of the principles of modern chemical and physical science, and especially of colloidal behavior, is the youngest in the industrial advance of this generation. Glue has always been a colloidal material, but only today has it become possible to make deliberate and directive application of the knowledge which we have of the colloid state to a more intelligent control of manufacturing processes.

<sup>30</sup> *J. Am. Chem. Soc.*, **44** (1922), 464.

<sup>31</sup> *Am. Chem. Soc. Meeting*, Sept. 5-9, 1922.

<sup>32</sup> *J. Am. Chem. Soc.*, **44** (1922), 2633; **45** (1923), 3139.

<sup>33</sup> *J. Am. Chem. Soc.*, **46** (1924), 852.

## CHAPTER XXXII

### COLLOID CHEMISTRY AND THE PHOTOGRAPHIC PROCESS

By

S. E. SHEPPARD

In a sense it might be said that photography has been dependent upon colloids and colloid chemistry from its earliest days. The discovery of N. de Niépce that asphaltum exposed to light becomes insoluble, thus permitting an image to be formed by dissolution of the unexposed portions with organic solvents, might be regarded as based on "selective peptization." Again, the more practically important discovery by Daguerre that a silver mirror fumed with iodine vapor gave an invisible image which could be developed by exposure to mercury vapor is evidently founded on "selective adsorption." Such baptism of the first fruits of photography into the orthodox colloid denomination must suffice to deal with them. A closer examination would show a more substantial relation to colloid chemistry, but we cannot delay. Again, the early use of so colloidal a material as paper as a substratum or matrix for silver salts might be heralded as introducing colloids into photography. However, the veritable sponsor of unquestionable—till recently—colloids in the art was Niépce de St. Victor, nephew of the colleague of Daguerre, who about 1847 not only used glass as a support, but employed a variety of bio-colloids<sup>1</sup> as vehicles for the sensitive substances—soluble and insoluble salts of silver. Mostly it was silver iodide, with excess of silver nitrate, which was used for "printing out." Niépce experimented at first with *starch* as a vehicle, then tried *gelatin*, but rejected it because too soluble in the acid silver sensitizing bath. He then came to use *albumen*, with which various hygroscopic substances, such as sugar, honey,

<sup>1</sup> Termed by Dumas in 1830, "*matières organisées*," as distinguished from definite "*matières organiques*." (Traité de Chimie, vol. 5.)



dextrin, etc., were incorporated to increase its permeability and ease of working both in sensitizing and development. About this time (1850 to 1860) *casein* and (wheat) *gluten* were also used as vehicles. While albumen survived for some time for positive processes, it was soon displaced for negative processes by *collodion* (pyroxylin, or cellulose nitrate). Although first suggested by G. le Gray in 1850, the first practical prescription was due to F. Scott Archer of London, in 1857. The "wet plate" process, using silver iodide, sensitized with excess silver nitrate, in collodion, and developed with an acid silver developer,<sup>2</sup> was due fundamentally to Talbot, and Scott Archer. Collodion was again almost entirely displaced for negative processes, and largely for positive ones, by *gelatin*, in the gelatin emulsion process due to Dr. Maddox (1871), Kennet, and Bolton (1874).

So much for the concrete introduction of typical colloids into the art of photography. The equally important introduction of the science of photography to the abstract realm of colloid chemistry was actually accomplished by M. Carey Lea (1889), for all that he regarded his colloid silver preparations as "allotropic" silver modifications, and his colloid photohalides as "lakes" of silver subhalide on normal halide. It is a great merit of Dr. Lüppo-Cramer to have rescued Lea's fundamental work, if not from oblivion, at any rate from neglect and oversight. His German edition<sup>3</sup> of Lea's papers is the most accessible and only independent edition.<sup>4</sup> After Lea, many photographic experimenters and chemists continued to be colloid chemists without knowing it. However, with the general increase of interest in colloid chemistry, its development and applications, there soon followed recognition of its important rôle in photography. In consolidating this viewpoint, and in a variety of

<sup>2</sup> That is, a solution of silver nitrate with an acid reducer, *e.g.*, ferrous sulfate plus acetic acid, or gallic acid plus citric acid.

<sup>3</sup> LEA, CAREY: "Kolloides Silber und die Photohaloide," (in deutscher Übersetzung von Dr. Lüppo-Cramer, Dresden, 1908, Th. Steinkopf).

<sup>4</sup> It is little to the credit of American and English photographers that this should be so. The recent publication of the Hurter and Driffield Memorial Volume by the Royal Photographic Society (1920) suggests the desirability of a similar tribute in the shape of a Carey Lea Memorial Edition, including both his practical contribution to photography, as well as his scientific ones.

contributions to the colloid chemical viewpoint of photographic processes, we should again cite Dr. Lüpke-Cramer as preeminent, and refer our readers to his works for more extensive discussions of the subject.<sup>5</sup> Certain other general articles and works on special phases may also be cited at this point.<sup>6</sup>

### SILVER HALIDE EMULSIONS

What is termed an "emulsion" in photography is actually a suspension of silver halide particles in a colloidal vehicle, such as collodion, albumen, but, most generally, gelatin. The import of colloid chemistry for these emulsions is much more considerable than the sole use of such vehicles. Apart from the crass but important fact of the concentration of the silver halide, the greater number of the typical factors in the preparation, as in the final product, are of colloid chemical character. Such are the conditions determining, and the value of, the grain size, or the "dispersity," the importance of adsorption, of surface tension phenomena, of viscosity.

Technically, sensitive silver halide emulsions are divisible into two main classes or groups:

1. The silver halide is precipitated in the presence of excess of soluble silver salt, *e.g.*, *silver nitrate*. This group includes "wet collodion," still extensively employed in photomechanical work, collodion emulsions for printing-out. The excess soluble silver salt is supposed to act as a chemical sensitizer, *i.e.*, as a halogen absorbent. More recently, a different rôle has been imputed to it. This will be referred to later.

2. The silver halide is precipitated in the presence of excess of *soluble halide*, *e. g.*, potassium bromide. This group comprises both positive and negative emulsions for development. Here,

<sup>5</sup> "Kolloidchemie und Photographie," 1st ed. 1908; 2nd ed. (chiefly new matter) 1921, Th. Steinkopff, Dresden; also "Photographische Probleme," 1907, W. Knapp, Halle; "Das Latente Bild.," 1911, W. Knapp, Halle.

<sup>6</sup> SHEPPARD, S. E.: Colloid chemistry in relation to photography, *Phot. J.*, **49** (1909), 320; SLADE, R. E.: Colloid chemistry in photography, in *Third Report on Colloid Chemistry* (Brit. Assoc. Report, published by H. M. Stationery Office, London, 1920); TRIVELLI, A. P. H. and SHEPPARD, S. E.: "The Silver Bromide Grain of Photographic Emulsions," Eastman Kodak Co., and Van Nostrand, 1921; SHEPPARD, S. E.: "Gelatin in Photography," vol. 1, Eastman Kodak Co., and Van Nostrand, 1923.

the excess of soluble halide is usually more or less completely washed out before the emulsion is coated; it is operative in the formation of the precipitate, conditioning the recrystallization of the silver halide as a solvent.

In principle, the two classes of emulsions may be regarded as derived from the two types of silver halide hydrosols, which are obtainable in very dilute solutions, stabilized either by a slight excess of silver ions or of halide ions.<sup>7</sup> These stabilizing ions are adsorbed to the surface of the silver halide particles; in view of their crystalline character, as disclosed by *x*-ray spectroscopy for even the ultramicroscopic ones, one may consider them as attached by electrostatic forces to a surface layer of ions of opposite charge of the crystal lattice. Adsorption and peptization go hand in hand here, since this adsorption is only a phase of the formation of soluble double salts, or complex compounds. In the series



adsorption, peptization, and double salt formation by excess silver nitrate, or excess soluble halide, increases in facility as we pass from the chloride to the iodide.

Simple silver halide hydrosols prepared without protective colloids have more of a theoretical than a practical interest for photography. They may be prepared, as stated, from dilute solutions of the reactant, *e.g.*, for AgBr, at concentrations below 0.001 normal. Layers of silver bromide prepared from these by sedimentation have been used by Herschell,<sup>8</sup> by K. Schaum,<sup>9</sup> H. Weiss,<sup>10</sup> and others for theoretical investigations, and by V. Schumann<sup>11</sup> for plates sensitive to the ultra-violet. Schumann, however, used an undercoating of gelatin to hold the particles. It is possible to prepare in this way layers giving both print-out (visible) and developable (latent) images. In the latter case, however, many precautions are necessary, if the chemical reducing agents used in developing the image are not

<sup>7</sup> LOTTERMOSER, A.: *J. prakt. Chem.*, N. F., **56** (1897), 241; **71** (1905), 296.

<sup>8</sup> Sir J. Herschell; *cf.* HUNT, R.: "Researches on Light," London, 1854, p. 66.

<sup>9</sup> Eder's *Jahrb. Phot.* (1904), 74.

<sup>10</sup> *Z. physik. Chem.*, **54** (1906), 322.

<sup>11</sup> *Sitzb. Akad. Wiss. Wien. Abt. 2a*, **102** (1893), 994.

to reduce the silver halide immediately. In (incompleted) investigations on such layers, the author found it desirable to mix the reagents and sediment out in a vessel similar to that used for the anaerobic culture of bacteria. Only dust-free air was allowed in the chamber; all washing and treatment of the sediment was done in the same enclosed chamber. This had to be carefully protected from vibrations during sedimentation, and the silver nitrate specially prepared and tested for freedom from traces of colloid silver. For most purposes, the silver halide hydrosols prepared in the presence of gelatin are more instructive, as well as easier to operate. Actually, the emulsions used in Lippmann interference photochromy, so-called grainless emulsions, are of this type. Lüppo-Cramer<sup>12</sup> has given a useful prescription for a "grainless" emulsion allowing some interesting experiments. Mix together 300 cc. each of 10 per cent gelatin solution containing respectively 6 g. of silver nitrate and 4.5 g. of potassium bromide, at about 35 to 40°C., and maintain at this temperature. The straight silver bromide hydrosol is easily flocculated by electrolytes, especially polyvalent cations, such as  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ , etc., whereas the gelatino-silver bromide sol is protected against these. It is, however, still subject to reduction of dispersity by certain reagents, notably silver bromide solvents, such as ammonia and soluble bromide. By the addition of a little ammonia to the "grainless" emulsion described above, and heating a short time nearly to boiling, the formerly clear sol becomes opaque, and, on prolongation of the treatment, visibly "grainy."

This *ripening* is partly a flocculation but chiefly a recrystallization phenomenon, supposedly due to the solution of smaller crystals and redeposition on larger ones of lesser solubility. The application of this principle, due to Ostwald, to the growth of crystals, has been frequently discussed, but insufficiently studied on the experimental side.<sup>13</sup> This ripening of the grainless emulsion results in a great increase of photographic sensitiveness, which may be increased some 500 or more times in this way.

<sup>12</sup> "Kolloid-chemie u. Photographie," 2nd ed., p. 14.

<sup>13</sup> Cf. TRIVELLI, A. P. H. and SHEPPARD, S. E.: "The Silver Bromide Grain of Photographic Emulsions," p. 57, Eastman Kodak Co., and Van Nostrand, New York, 1921.



While such alteration of grain by after-treatment plays a considerable rôle with the slower positive emulsions, the grain size of the faster negative emulsions is determined by other factors. It must be noted that at high magnifications (1,000 to 2,500 diameters) the silver bromide grains of these emulsions are found to be definite crystals<sup>14</sup> of various shapes and sizes. These relatively coarse-grained negative emulsions are not produced from fine-grained emulsions by ripening, but the grain size is determined by the conditions of initial precipitation. High concentration of the reactants ( $\text{AgNO}_3$  and  $\text{KBr}$ ), low concentration of gelatin, high temperature of mixing, and retarded addition permit the process of recrystallization to take place at once with the formation of definite, coarse-grained suspensions.<sup>15</sup>

The dispersity of the silver halides in photographic emulsions may be judged by the statement that in positive<sup>16</sup> emulsions the particles seldom exceed  $0.3\mu$  in diameter, in negative emulsions, 3 to  $4\mu$ . These are maximum sizes, the averages being much less. In negative emulsions the *distribution* of grain sizes, or, statistically, the grain-size frequency curve, is of great importance for the photographic characteristics. Recent investigations<sup>17</sup> have shown that the size-frequency curves of most emulsions can be expressed by probability formulas, either of exponential or (modified) Gaussian type. The unquestionable correlation of high sensitiveness of developable emulsions with coarse grain is not entirely cleared up, but the more recent contributions to its explanation will be noticed in connection with the latent image. It only remains to state that these silver bromide crystals belong to the regular system, as do also the silver iodobromide grains, containing several per cent silver iodide. In some emulsions the grains are nearly spherical, in others, mostly flat tablets of hexa-

<sup>14</sup> BANKS, E.: *Phot. J.*, **22** (1898), 159; BELLACH, V.: "Struktur d. phot. Neg.," 1903; LÜPPO-CRAMER: "Photog. Probl.," 1907, p. 51; TRIVELLI and SHEPPARD: *Op. cit.*

<sup>15</sup> These must not grow too rapidly, however, and throw out the precipitate.

<sup>16</sup> Not including lantern slide and cinematograph positive, in which the grain size seldom exceeds  $1\mu$ .

<sup>17</sup> WIGHTMAN, E. P., TRIVELLI, A. P. H. and SHEPPARD, S. E.: *J. Phys. Chem.*, **27** (1923), 1, 141, 466.

gonal and triangular shape, of thickness about one-fourth to one-half their diameter.

### VEHICLES AND PROTECTIVE COLLOIDS

The function of the binding or suspending medium of the photographic emulsion layer is partly that of a mechanical binder, but primarily that of a *protective colloid*. As such, it has a marked influence upon the process of aggregation of a new phase out of solution; the great importance of this was only realized after some time. The progress of photography with silver salts has depended in a large measure upon the displacement of *albumen* by *collodion*, and of *collodion* by *gelatin*. Although collodion and gelatin are both still used, the latter is much the more important. Collodion is a solution of nitrated cotton (cellulose) in a mixture of ethyl ether and ethyl alcohol. The cellulose nitrates used for collodions must be practically entirely soluble in a mixture of equal parts of these solvents. The percentage of nitrogen may vary from about 10.8 to 13 per cent, but this alone does not determine the solubility and viscosity. These are affected much more by variation of the water content of the mixed nitric and sulfuric acids used for nitration, by changes in the temperature of nitration, and of the quality of cotton cellulose employed. A collodion for "wet plate" work may contain about 1.5 per cent dry cellulose nitrate, and have a viscosity about 10 times that of water. This will give it sufficient body to flow evenly yet readily over quite large plates. On evaporation of the solvents it should form a clear elastic film, which should be strong enough to withstand after-operations, but should not rapidly become horny and impermeable. Neither the solution of cellulose nitrate nor the solvents should reduce alcoholic ammoniacal silver nitrate solution in the dark in 9 hours. If the nitrating acids have not been washed out sufficiently, the solution will become more acid and rapidly lose viscosity. A certain amount, about 5 per cent, of water can be added to collodion without causing precipitation, but it is precipitated by excess, and this has been used to purify it. The collodion film as first formed is fairly permeable to water and dissolved substances, but only swells slightly, differing in this from gelatin. Collodion is used as "wet collodion," and in collodion emulsion. In the former,

still considerably used for photomechanical reproduction purposes, an "iodized" collodion is prepared, containing a mixture of, *e.g.*, cadmium and strontium iodides, with a little strontium bromide, these salts being fairly soluble in alcohol. This solution is flowed over a glass plate before use, and when the solvent has evaporated, the film is sensitized with silver nitrate solution.

This is usually saturated with silver iodide before use. Otherwise, by using a somewhat concentrated silver nitrate solution, an interesting example of *periodic precipitation* can be observed on iodized collodion. On bathing in the silver nitrate solution the first formed precipitate will redissolve, as stronger silver nitrate diffuses in, then reappear, and sometimes repeat this performance.

The latent or invisible image on "wet collodion" is developed with an "acid silver" developer, *e.g.*, silver nitrate plus ferrous sulfate and acetic acid. An interesting example of colloid chemical principles was foreshadowed in Hardwick's "Photographic Chemistry" (seventh edition, page 267). He observed that overexposure produced a warmer toned image than normal exposure. This is due to the greater number of nuclei for development produced by increased exposure, and the consequent finer grains of the silver particles produced on development. The developed image on wet plate negatives is almost entirely superficial, and easily mechanically injured, for which reason it is usually protected by varnishing. The chief value in the process consists in the freedom from "grain" of the image. The structure of the silver image will be referred to again later. Collodion has much less protective power than gelatin, and this is manifest in the preparation of collodion emulsions, when impurities or slight errors in manipulation readily lead to flocculation of the silver bromide or chloride. *Collodio-silver-bromide* emulsions, prepared with equivalent amounts of the silver nitrate and soluble bromide, are very insensitive. They may be sensitized by bathing in silver nitrate, or, according to Albert's process, color-sensitized with silver eosinate or silver erythrosinate. *Collodio-silver chloride* emulsions are considerably used for direct "print-out" papers, being sensitized with silver citrate.

Various substances, such as honey, tannins, resins, added to collodion emulsions as "preservatives," have been shown by Lüppe-Cramer to function by maintaining the permeability.

The typical emulsoid or solvated colloid gelatin<sup>18</sup> is of much greater importance for modern photography. Its greater protective action in regard to silver halides has already been mentioned. The diminution of the rate of reduction of, *e.g.*, silver chloride, in the presence of gelatin, was investigated by Reinders and van Niewenburg<sup>19</sup> and attributed not to interference with the primary reaction



but to retardation of the aggregation of the reduced silver atoms. We may note three principal functions of gelatin as a solvated colloid in photographic processes:

1. In the formation of the emulsion as a polydisperse system of silver halide grains.

2. In the inhibition of reduction in the absence of exposure to light or chemical "fogging" agents, and the regulation of reactions of reduction, etc.

3. As a reversible water-swelling hydrogel, permitting free diffusion of crystalloids.

It is to none of these alone, or conjointly, however, that the very high sensitivity possible with gelatino-silver bromide emulsions can be attributed entirely. It is well known to emulsion makers that different gelatins behave very differently as regards photographic properties, and that these differences can be accentuated by pretreatment of the gelatins.<sup>20</sup> For all the importance of large grains (see page 763) for high sensitivity, it may be shown that this alone is not determinative. The author and E. P. Wightman<sup>21</sup> have shown that emulsions of precisely the same average grain size and distribution of grain size (frequency) could be prepared, according to identically the same procedure, with different gelatins. Yet these emulsions had widely different photographic properties, speeds varying from 60 H. and D. (slow plate) to 500 H. and D. (fast plate) being obtained. Con-

<sup>18</sup> With due respect to the contentions that we have to do here with nothing but an amphoteric electrolyte.

<sup>19</sup> *Kolloid-Z.*, **10** (1912), 36.

<sup>20</sup> *Cf.* SHEPPARD, S. E.: "Gelatin in Photography," vol. 1.

<sup>21</sup> Paper contributed to Symposium on Photographic Chemistry, Faraday Society, 1923.



versely, it is possible to convert a high-speed plate to a slow plate by desensitizing with an oxidizing agent, such as chromic acid, or persulfate, or permanganate.<sup>22</sup> Hence, it must be concluded that the sensitivity and other photographic properties are chiefly determined by the balance of the sensitizing and desensitizing action of the gelatin.<sup>23</sup> It is very likely that the sensitizing consists of a very minute amount of reduction of the silver halide to amicroscopic nuclei of colloid silver (of which more later), though this cannot be regarded as certain.

Returning to the more definitely colloidal properties of gelatin in photographic processes, both the functions (1) and (2) noted above may be attributed to adsorption of gelatin to the surface of the particles of the newly formed phase. In the process of emulsion making, and again in the coating of the emulsion on supports, the viscosity of the gelatin sol is important. Valuable investigations of this property have been made by J. Loeb,<sup>24</sup> E. T. Oakes and C. E. Davis,<sup>25</sup> and R. H. Bogue.<sup>26</sup> While Oakes and Davis consider that there is a definite temperature of transition between sol and gel forms, Bogue concludes, from measurements of the incidence of plastic yield, that the temperature is not fixed but depends upon the concentration of the sol. Results obtained by the writer and his collaborators<sup>27</sup> confirm Bogue's result as regards plasticity (in the sense of Bingham's work). An 8 per cent solution exhibited plastic flow below 35°C. but not above, a 4 per cent at 28°C. but not at 30°C., a 2 per cent at 25°C. but not at 28°C. These values again depended upon whether the solution of given concentration was prepared by diluting a more concentrated one, or directly, indicating a different structure in the two cases.

The work of J. Loeb has shown the fundamental importance of the hydrogen ion concentration for the properties of the

<sup>22</sup> *Ibid.*: cf. also LÜPPO-CRAMER: "Phot. Mitteilungen," 1909, p. 328.

<sup>23</sup> Cf. SHEPPARD, S. E.: *J. Ind. Eng. Chem.*, **14** (1922), 130.

<sup>24</sup> LOEB, J.: "Proteins and the Theory of Colloidal Behavior, McGraw-Hill Book Co., N. Y., 1922.

<sup>25</sup> OAKES, E. T. and DAVIS: *J. Am. Chem. Soc.*, **44** (1922), 464.

<sup>26</sup> BOGUE, R. H.: *J. Ind. Eng. Chem.*, **14** (1922), 32; *J. Am. Chem. Soc.*, **44** (1922), 1313, 1343.

<sup>27</sup> Physical Chemistry of the Photographic Process, *Trans. Faraday Soc.*, **19** (1923) No. 56.

ampholyte gelatin. Photographically, the H ion value is of less importance in the earlier stages than in the later ones of the photographic process. The process of development is generally carried out in alkaline solutions of a pH about 8 to 10, which is near the pH of maximum jelly strength for a chilled jelly of given concentration.<sup>28</sup> In absence of the electrolyte this would mean a high degree of swelling, but the concentrations of salts such as  $\text{Na}_2\text{SO}_3$  and  $\text{Na}_2\text{CO}_3$  in the developer repress the swelling. The actual swelling is limited, by the attachment of the layer and a rigid support, to the direction normal to the support. Measurements of the rate of swelling in ordinary developing solutions<sup>29</sup> show that the maximum swelling is not more than 3 to 6 times the original thickness. When the plate is transferred to water, the swelling increases somewhat, but on again transferring to the usually acid fixing bath (at about pH 4) the gelatin has to pass through the isoelectric point (at pH 4.7). A considerable strain is thus thrown on the gelatin structure (since all swelling and contraction is limited to one direction). The author and F. A. Elliott<sup>30</sup> have shown that protraction of this beyond the elastic limits, and liberation of tangential stresses in the jelly layer, probably account for the curious puckering or reticulation sometimes produced. For other phenomena associated with swelling in photographic solutions, reference may be made to papers by the author and his collaborators.<sup>31</sup> The hardening and tanning of gelatin in such solutions is noted in a later section (see page 777) of this chapter. As regards the converse process of drying, this is regulated chiefly by the rate of diffusion of water in the gelatin layer to the evaporating surface. Consequently, it progresses more rapidly at corners and edges, and proceeds by a gradual regression of moist area to the center of a plate or film.

#### VISIBLE AND LATENT IMAGES WITH SILVER HALIDES

At the present time it would be almost permissible to paraphrase the title of this section by "dispersions of colloid silver in silver halides." The three silver halides,  $\text{AgCl}$ ,  $\text{AgBr}$ , and

<sup>28</sup> Cf. SHEPPARD, S. E. and SWEET, S. S.: *Ind. Eng. Chem.*, **15** (1923), 571.

<sup>29</sup> SHEPPARD, S. E.: *J. Ind. Eng. Chem.*, **14** (1922), 130.

<sup>30</sup> *J. Ind. Eng. Chem.*, **10** (1918), 727.

<sup>31</sup> *J. Am. Chem. Soc.*, **44** (1922), 373.

AgI, all darken on exposure to light, and it has been demonstrated that halogen is given off, although the amount is very small, even on prolonged exposure. The nature of the visible images thus produced long remained uncertain. Their high resistance to oxidizing agents and silver solvents, such as nitric acid, was supposed to preclude metallic silver, although as early as 1857 Guthrie suggested that it might be silver in a "passive" form. It was preferred to regard them as subhalides, generally given the formula  $\text{Ag}_2\text{X}$ , although only in the case of subfluoride,  $\text{Ag}_2\text{F}$ , was definite evidence of the existence of such compounds afforded. In 1889, M. Carey Lea<sup>32</sup> showed that it was possible to prepare, by processes of incomplete chemical reduction of the silver halide, and subsequent extraction with silver solvents, varicolored substances having a slight excess of silver over that required by the formula  $\text{AgX}$ . These had the stability and all the properties of the silver halides colored by light, and both were termed indifferently by Lea "photohalides." Lea regarded them as "lakes" of silver subhalide and normal halide, compounds of indefinite combining proportions, depending upon the conditions of preparation. Lea also discovered methods of preparing silver in various "soluble allotropic forms" of various colors, and made the further suggestion that silver in the photohalides is present as allotropic silver. On the synthetic side, subsequent investigation has added little to Lea's brilliant solution of the nature of the photohalides. It has, however, shown that his "allotropic" silver modifications consist of colloid silver, and that the photohalides are adsorption compounds of colloid silver and silver halide. The constitution of the photohalides and of the print-out on visible images with silver compounds has become, therefore, a problem of colloid chemistry applied to photography.

In this demonstration, Lüppo-Cramer<sup>33</sup> and R. Lorenz<sup>34</sup> have given the most important evidence. The former found that if a hydrosol of silver halide is mixed with a colloid silver sol, the mixed sol coagulated, *e.g.*, by dilute sulfuric acid, and then extracted with strong nitric acid, that varicolored red, blue, or violet *photohalides* are obtained, identical with Lea's photohalides, and

<sup>32</sup> *Op. cit.*

<sup>33</sup> *Op. cit.*

<sup>34</sup> *Z. anorg. Chem.*, **91** (1915), 57.

containing, according to the mode of preparation, slight excess, not more than fractions of a per cent, of silver over that of normal halide. Lüppo-Cramer further succeeded in producing regular gelatin emulsions of these photohalides by peptizing with a silver halide solvent and dispersing in gelatin. Such emulsions enable a number of photographically significant reactions to be carried out, of which more later. Lorenz and W. Eitel<sup>35</sup> prepared optically clear silver halides by fusion in the presence of halogen. On exposure to the light in an ultramicroscope, the crystals, at first clear, begin to darken, and soon show ultramicroscopic particles which grow rapidly in the light, and even in darkness, if heated to 300°C. The metallic "nebula" and particles produced by light are quite analogous to those produced in the electrolysis of fused salts.

Reinders<sup>36</sup> observed that silver chloride, crystallized from an ammoniacal solution containing colloidal silver, was colored by this, thus forming crystallized photohalides. In the presence of small amounts of gelatin, the latter was taken up by the crystallizing halide, but not by the colloid silver. The gelatin-containing chloride was more sensitive to light than the chloride when crystallized alone.

The "disperse" character of the photochemical decomposition in silver bromide observed by Lorenz was confirmed by photomicrography by Trivelli and Sheppard.<sup>37</sup> Recently they have shown that in selected crystals the decomposition, starting at isolated points, tends to follow the directions of most rapid growth of the crystal.<sup>38</sup>

It appears, from work to be noted shortly, that the dispersion of the visible photochemical decomposition in silver halide crystals is foreshadowed in the latent image. From the fact that the change at this stage is too minute to be determined directly, the nature of the latent image has been even more a matter of dispute than that of the visible image, although the most natural conception is to consider it identical with the sub-

<sup>35</sup> *Ibid.*, **92** (1915), 27.

<sup>36</sup> REINDERS, W.: *Z. Chem. Ind. Koll.*, **9** (1911), 10.

<sup>37</sup> "The Silver Bromide Grain of Photographic Emulsions," Van Nostrand, 1921, pp. 83-84.

<sup>38</sup> *Phot. J.*, **63** (1923), 334.



stance of the visible image, but quantitatively less. However, various hypotheses which regarded the change as purely physical have been put forward, which it is not necessary to consider here.<sup>39</sup> The theory which agrees best with the reactions of the latent image regards it as an early stage of photohalide formation *i.e.*, as a dispersion of colloid silver in silver halide. This accounts equally for the acceleration of reduction, shown in developability, and for the effect of oxidizing agents. By treatment with chromic acid (2 per cent  $\text{CrO}_3$  plus 1 per cent  $\text{H}_2\text{SO}_4$ ) the latent image is destroyed, as regards chemical development. However, if considerable overexposure—say 20 times normal—is given, and the plate first fixed, *i.e.*, the silver halide removed by “hypo,” an image can be developed by an acid silver developer. This was attributed by Sterry<sup>40</sup> to the existence of an organic latent image, an effect on the gelatin (or collodion), but Lüppo-Cramer<sup>41</sup> has shown that it is more simply explained as colloid silver formed *inside* the grain, on high exposure. This is normally protected by silver halide, so that when the surface latent image is removed by oxidizing agents, the internal nuclei cannot initiate reduction with a developer. By removing the protecting silver halide, these nuclei become active and can attract silver from a supersaturated solution. Lüppo-Cramer has shown that synthetic photohalides behave quite similarly. If the excess silver is not removed with too strong an oxidizer, they are immediately developable, but treatment with chromic acid removes this, making them no longer reducible.

It was observed by R. Luther and W. A. Uschko<sup>42</sup> that if plates or films (certain papers show the effect) were exposed liberally to X-rays, then to ordinary light, that the X-ray image was “developed” as a pinkish coloration, in contrast with the grey-green tone of the untreated silver bromide. This reaction is much favored by the presence of sulfite or nitrite in the emul-

<sup>39</sup> Cf. SHEPPARD, S. E. and MEES, C. E. K.: “Investigations on the Theory of the Photographic Process.”

<sup>40</sup> *Phot. J.*, **22** (1898), 264.

<sup>41</sup> “Photo. Probleme.”

<sup>42</sup> *Phys. Z.*, **4** (1903), 866; also Zehnder: *Ann. Phys.* (4), **12** (1903), 413; and VILLARD, M. P.: “Actions Chimiques des Diverses Radiations,” Paris, 1900.

sion. It has been explained by Lüppo-Cramer<sup>43</sup> as due to the higher dispersity of the colloid silver in the grains exposed to X-rays. On further exposure to ordinary light, the much greater number of nuclei per grain give a redder tint, since the color of colloid silver sols follows the order yellow  $\rightarrow$  brown  $\rightarrow$  red  $\rightarrow$  purple  $\rightarrow$  blue  $\rightarrow$  grey with increasing size of particle. This reaction recalls the so-called Becquerel effect. E. Becquerel observed in 1840 that if silver chloride was exposed a short time to blue or violet light, then to yellow light, that this "developed" up the image. Lüppo-Cramer<sup>44</sup> has shown this to be due to the color-sensitizing powers of colloid silver. The "red sensitizing" of ordinary silver bromide emulsions by treatment with bisulfite<sup>45</sup> and with iodides and cyanides<sup>46</sup> is also probably due to formation of colored colloid silver—either by fresh reduction, or by a "ripening" action on previously existent silver amicrons.

Not only are the visible and latent images to be attributed to colloid silver absorbed, and to some extent in solid solution in silver halide, but it is likely that much of the sensitivity of the silver halide grain is due to the same. There have been many suggestions that part of the "ripening" process (see page 762) consists in a very slight reduction of the grain. Trivelli and Sheppard<sup>47</sup> found that on fuming gelatino-silver bromide with ammonia, traces of colloid silver are formed, and Lüppo-Cramer<sup>48</sup> showed that on treating ripened plates with a silver solvent, such as the chromic acid solution used in destroying the latent image, they become greatly desensitized. The writer, E. P. Wightman and A. P. H. Trivelli have recently investigated this microscopically on one-grain layer plates, using a definite technique to remove traces of chromic acid previous to exposure (since otherwise apparent desensitizing might be due to destruction of nascent latent image) and find that smaller grains are relatively more desensitized than large ones.<sup>49</sup> This definitely establishes

<sup>43</sup> Das Latente Bild," p. 10.

<sup>44</sup> *Idem.*

<sup>45</sup> CAPSTAFF, J. G., and BULLOCK, E. R.: *J. Frank. Inst.*, **190** (1920), 871.

<sup>46</sup> RENWICK, F. F.: *Phot. J.*, **61** (1921), 12; SHEPPARD, S. E.: *Ibid.*, **62** (1922), 88.

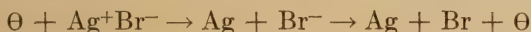
<sup>47</sup> *Op. cit.* Ref. 37.

<sup>48</sup> *Phot. Mitt.*, *loc. cit.*

<sup>49</sup> *J. Frank. Inst.*, **195** (1923), 675.

the fact that the "sensitive spots" deduced by Svedberg<sup>50</sup> from his extension of Hodgson's observation exist prior to exposure.

F. F. Renwick<sup>51</sup> has suggested that in high-speed emulsions the action of light is limited to a reduction in the dispersity of preexistent silver amicros to particles large enough to function as nuclei for reduction on development. F. Weigert<sup>52</sup> has made a somewhat similar suggestion as regards the growth of the visible image on print-out emulsions. The writer is more inclined to consider the sensitizing effect of colloid silver particles as due to the lower energy required to release an electron from metallic silver than from a silver halide lattice, held together by the electroaffinity of the ions. The liberated electron could effect a certain limited chain reaction



producing a decomposition of AgBr limited by the initial energy of the released photoelectron. As he has pointed out elsewhere,<sup>53</sup> the sensitizing function of colloid silver in the silver halides is possibly quite analogous to the effect of traces of bismuth, copper, etc., in developing phosphorescence in the alkaline earth sulfides.

#### DEVELOPMENT AND THE DEVELOPED IMAGE

The development of the silver halides is, in principle, a simple ionic reaction, typified by the equation



*i.e.*, conversion of silver ions to metallic silver. This simple reaction equation is, however, far from expressing the innumerable complexities of the actual process. Since the reaction occurs in a polydisperse microheterogeneous system, and the product is

<sup>50</sup> *Phot. J.*, **62** (1922), 186.

<sup>51</sup> *J. Soc. Chem. Ind.*, **39** (1920), 156T.

<sup>52</sup> *Sitzb. preuss. Akad. Wiss.* (1921), 641-650; *cf. also Physik. Z.*, **22** (1921), 674; *Z. Physik. Chem.*, **99** (1921), 499; EGGERT, J. and NODDACK, W.: *Sitzb. preuss. Akad. Wiss.* (1921), 631.

<sup>53</sup> "The Silver Bromide Grain, etc.," 1921, p. 51.

also polydisperse, many of the phenomena are of colloid chemical character. Technically, two types of development are distinguished, so-called "physical" development, in which the silver which builds up the developed image upon nuclei furnished by the latent image is furnished from soluble silver salt in the developing solution, and "chemical" development, in which the silver is formed by reduction of the solid silver halide grains themselves in which nuclei are present. In the former case, owing to the higher concentration of silver ions, the reduction potential is low, reducers in acid solution being used. In the latter case, higher reduction potentials are employed, the solutions being alkaline.<sup>54</sup> To this it may be added that with very fine-grained silver bromide emulsion, and chloride emulsions, such as are used in positive processes and developing out papers,—since the developer contains sufficient sodium sulfite to exercise considerable dissolving power upon these halides,—development here, though in alkaline solution, approaches the so-called "physical" type.

The action of the latent image, considered as colloid silver nuclei, in initiating reduction of contiguous silver salt, is a case of heterogeneous catalysis. In the case of physical development from an acid silver solution, as in wet collodion, the silver image is practically entirely on the surface; it is very fine-grained and compact, approaching "mirror silver" deposited from silvering solutions. In alkaline chemical development the use of highly restrained developers, particularly when containing silver halide solvents, also produces a compact, fine-grained deposit. On the other hand, the normal alkaline development of negative emulsions produces a more open, spongy, black silver grain, and this difference of the gel character of the developed image is responsible for certain phenomena in after-treatment. R. Liesegang and Lüppo-Cramer<sup>55</sup> have broadly distinguished between the two types as "grain-surface" and "grain-volume" development, on the assumption that in the former case everything depends upon the number of nuclei on the surface of the grain,

<sup>54</sup> On the physical chemistry of development, see SHEPPARD and MEES: "Theory of the Photographic Process," and NIETZ, A. H.: "The Theory of Development," Eastman Kodak Co., and Van Nostrand, New York, 1922.

<sup>55</sup> LIESEGANG, R.: "Photochem. Studien," Dusseldorf, 1895, p. 177; LÜPPO-CRAMER: *Phot. Korr.* (1908), 453.



but not in the latter. This distinction is, however, somewhat too sweeping. In the ordinary chemical development of coarse-grained silver bromide, it was shown microscopically by M. B. Hodgson<sup>56</sup> that development starts at isolated points, which increase in number and grow together as development proceeds. Since treatment with oxidizing agents after exposure (such as chromic acid, permanganate, etc.) prevents chemical development, it is evident that this is initially a "grain-surface" reaction, and the subsequent progress to the spongy black silver grain or the compact finer grain is chiefly a matter of the reduction potential of the developer and the presence of complex-forming silver halide solvents. If a silver bromide plate is exposed to light, then treated with chromic acid, no image can be obtained with a physical developer. If, however, after the chromic acid, the plate is bathed a short time in 0.5 to 1 per cent potassium iodide solution, an image can then be developed with a physical developer. Lüppo-Cramer,<sup>57</sup> who discovered this interesting reaction, attributes it to "exposure of nuclei" (*keimblosslegung*). The conversion of the AgBr grain to AgI disintegrates the grain (as can be observed microscopically) and is supposed to "lay bare" occluded colloid silver nuclei. The writer is inclined to attribute at least part of the action to the much greater adsorptive power of AgI, particularly for silver salts, as compared with AgBr. In the case of the acceleration of chemical development with low potential developers (as hydroquinone) by very dilute iodide solutions (1/1,000 to 1/100,000 normal) he has suggested<sup>58</sup> that the acceleration is entirely due to increased adsorption of the organic reducer, rather than to "*keimblosslegung*." Be that as it may, it is certain that the original existence of iodide in the silver bromide grain, introduced in the process of formation, brings about many of the properties caused by subsequent introduction.<sup>59</sup> In these cases the effects cannot be due to mechanical disintegration. They must rather be associated with a relatively weak adsorption of colloid silver to silver

<sup>56</sup> *J. Frank. Inst.*, **184** (1917), 705.

<sup>57</sup> *Kolloid-Z.*, **12** (1912), 42; also "Kolloidchemie und Photographie," 2nd ed., p. 63.

<sup>58</sup> SHEPPARD, S. E. and MEYER, G.: *J. Am. Chem. Soc.*, **42** (1920), 689.

<sup>59</sup> Cf. SHEPPARD, S. E.: *Phot. J.*, **62** (1922), 88.

iodide, which is borne out by the distinctive behavior of the photoiodide. In general, the stability of the photohalides diminishes in passing from AgCl to AgI.<sup>60</sup>

In a paper now in preparation, the author and his collaborators, E. P. Wightman and A. P. H. Trivelli, suggest that this is a consequence of the more compact arrangement of the atoms in the silver iodide crystal lattice, in consequence of which metallic silver atoms cannot be firmly keyed into the structure, as in the bromide and chloride. In any case, it is probable that *adsorption* of the reducer to the silver halide grain is the first phase of development.<sup>61</sup> The writer has suggested that the free silver ions of the crystal lattice hold ions of the reducer by electroaffinity, and the complex thus formed breaks down in the presence of colloid silver nuclei. W. D. Bancroft<sup>62</sup> considers that selective adsorption of the developer involves a greater or less peptization of the latent image, and that a transition from weakly peptizing, strongly reducing to strongly peptizing, weakly reducing developers exists. The furthest examples of the latter can give direct solarized or reversed images. He has found that by leaching with reducers used in development, in absence of alkali, *e.g.*, elon (metol), that developability can be destroyed. This has been also observed by Lüppo-Cramer and the writer has confirmed it. It seems questionable whether it is truly a peptization of the latent image as such which occurs here. What is more probable is a slight etching of the surface layers of the silver halide, the reducers in question having some tendency, greatest in the diamino bodies, like *p.* phenylene-diamine, to form soluble complexes with silver halides. The production of direct positives by development is associated with the formation of "dichroic fogs," colored forms of colloid silver produced when a solvent for silver halide is present in the developing solution.

Remarkable effects of certain dyestuffs, some in accelerating development, others in desensitizing the silver halides, so that development can be carried out in strong yellow or even white

<sup>60</sup> LÜPPO-CRAMER: "Kolloidchemie und Photographie," 2nd ed.

<sup>61</sup> Cf. SHEPPARD, S. E. and MEYER, G.: *J. Am. Chem. Soc.*, **42** (1920), 689.

<sup>62</sup> *Trans. Faraday Soc.*, **19** (1923) No. 56.

light, have been discovered by Lüppo-Cramer.<sup>63</sup> Here again selective adsorption no doubt plays a great part.

Colloidal phenomena due to the gelatin in development are chiefly connected with the diffusion process. A number of secondary phenomena in development are connected with the relative exhaustion of the developer in the lower layers, especially in the more exposed parts, due to diffusion lagging behind the reduction velocity. A special developer (amidol in weakly acid solution) has the property<sup>64</sup> of developing the back layers before the top ones. This is due to the gelatin combining with acid, and letting less acid and more strongly reducing amidol pass through.

#### FIXING AND HARDENING

Fixation consists in the removal of undeveloped silver halide by solvents, of which sodium thiosulfate ("hypo") is the most generally important, although potassium cyanide is still used to dissolve out the residual silver iodide of "wet collodion" plates. The principal colloid chemical factor in this stage of the photographic process is the influence of the concentration and H-ion content of the solutions on the swelling of the gelatin, and, reciprocally, the influence of the gelatin on the diffusion in and out of dissolved substances. If the time of fixation is plotted as a function of the concentration of thiosulfate, it is found that the time is a minimum for concentrations of around 35 to 40 per cent. Greater strengths of thiosulfate than this fix more slowly, the time increasing with the concentration. It can readily be shown<sup>65</sup> that this is due to the restriction of swelling of the gelatin, and of diffusion through it, so that, above the optimum, increased concentration delays rather than accelerates. The addition of substances tending to produce softening and peptization of gelatin, *e.g.*, ammonium thiocyanate, increases the speed of fixation at the optimum concentration of "hypo," but with danger of damage to the negative. The rate of fixation is chiefly governed by the diffusion out of the gelatin into the solution of

<sup>63</sup> Negativentwicklung bei hellem Lichte (Safranin-verfahren) Ed. Liesegang's Verlag M. Eger, Leipzig, 1921.

<sup>64</sup> Balagny.

<sup>65</sup> Cf. SHEPPARD, S. E., ELLIOTT, F. A. and SWEET, S. S.: Chemistry of the acid fixing bath, *J. Frank. Inst.* (July, 1923).

the soluble complex sodium silver thiosulfate.<sup>66</sup> A plate fixed in an inverted position, *i.e.*, emulsion down in the bath, fixes in about half the time of one lying, also at rest, with the emulsion side uppermost. The convection currents produced by the down-flow of heavy complex salt accelerate the diffusion process.

It is general in modern photography to use so-called "acid fixing baths." The tendency of acids to precipitate sulfur from thiosulfate is inhibited by using the weaker organic acids (acetic, citric, etc.) and by adding sodium sulfite to the thiosulfate. These acid baths have a hydrogen ion concentration of pH 4 to 5; the gelatin film, brought after brief rinsing from the alkaline developer at pH 8 to 10, is rapidly brought near or slightly beyond the isoelectric point, at the same time in the presence of relatively high concentrations of salts ( $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{SO}_3$ ). Consequently, the swelling is reduced to a minimum, and the tendency to dissolve by elevation of temperature is lessened. This effect, equivalent to raising the melting point of the jelly, is known photographically as *hardening*. The effect in this case is only a temporary one, disappearing as the films are washed. Permanent hardening, actually a tanning of the gelatin, is produced by definite hardening baths, which may, to some extent, be combined with the fixing bath. The substances generally used are potash alum ( $\text{K}_2\text{SO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ), chrome alum ( $\text{K}_2\text{SO}_4$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ), and formalin (solution of formaldehyde,  $\text{HCHO}$ ). Hardening agents of this type are generally added also, in various degrees, beforehand to emulsions. The hardening of gelatin by these substances is undoubtedly similar in principle to the tanning of the collagen of skins (leather formation). Chrome hardening (with chromium salts) is more effective than aluminum tanning. The action of these substances—to which may be added the similar effect of iron salts—has been explained on two different grounds. One view is that hydrolysis of the aluminum or other salt takes place in the gelatin, with the formation of hydrous (colloidal) oxides, which are adsorbed to the gelatin, and that it is this adsorption which effects the tanning.<sup>67</sup>

<sup>66</sup> Cf. SHEPPARD, S. E. and MEES, C. E. K.: "Theory of Photographic Process," p. 113.

<sup>67</sup> For the application of this in photographic chemistry see LÜPP-CHRAMER: "Kolloidchemie und Photographie," 1st ed., p. 121.



Another theory is that definite chemical combinations, aluminum, chromium, etc., gelatinates are formed, which are very slightly ionized (unlike sodium gelatinate, etc.) and do not swell.<sup>68</sup> It is considered possible that the combination is progressive, according as less or more of the metal is fixed by the gelatin. The formation of such gelatinates should not take place, in accordance with the amphoteric properties of gelatin,<sup>69</sup> at hydrogen ion concentrations corresponding to a  $\text{pH} < 4.7$ . The author and his collaborators<sup>70</sup> have investigated the influence of the hydrogen ion concentration upon the hardening of gelatin by aluminum and chromium salts, as shown by the melting point (temperature of solution of the gelatin). The problem is complicated by the progressive precipitation of the hydrous oxides with increasing  $\text{pH}$ , *i.e.*, increasing  $\text{OH}^-$ -ion concentration. In the case of alumina ( $\text{Al}(\text{OH})_3$ ) this commences to precipitate<sup>71</sup> at a  $\text{pH}$  of 3 but is not complete till  $\text{pH} = 7$  to 8, while at still higher values it commences to redissolve, forming *aluminates*.

Although such higher values of  $\text{pH}$  do not come into consideration for this phase of the photographic process, the amphoteric properties of the aluminum and chromium hydroxides complicate the question. According to the measurements made, if the gelatin jelly was hardened by an external bath of aluminum salt, the maximum hardening was affected at  $\text{pH}$  4, beyond which the hardening effect fell off rapidly again. The explanation of this, in the first instance, is that the precipitation of alumina had advanced, beyond  $\text{pH}$  4, to the formation of non-diffusible particles of hydrous alumina which would not penetrate the gelatin. It is curious, however, that the presence of citric acid, which keeps the alumina in solution—albeit as complex ion—did not alter this optimum value of the hydrogen ion concentration, although it greatly lessened the effective hardening. On the other hand, if the aluminum salt was mixed beforehand with gelatin solutions at various  $\text{pH}$  values, and the melting point of the jelly determined, the optimum  $\text{pH}$  was dis-

<sup>68</sup> PROCTER, H. R.: *Trans. Chem. Soc.*, **105** (1914), 313; PROCTER and WILSON, J. A.: *Ibid.*, **109** (1916), 307; Cf. Chapters I and II, this book.

<sup>69</sup> LOEB, J.: "Proteins and the Theory of Colloidal Behavior."

<sup>70</sup> *J. Frank. Inst.* (July, 1923).

<sup>71</sup> BLUM, W.: *Bur. Stand. Sci. Paper*, **286** (1916).

placed to pH 6. It appears probable from this that it is not  $\text{Al}^{+++}$  ions which combine with gelatin, but charged ionic micelles,<sup>72</sup> *e.g.*,  $\text{Al}(\text{OH})_2\text{Cl} \cdot (\text{Al}_2\text{O}_3)_x \cdot (\text{H}_2\text{O})_y$ , in general, positively charged, which neutralize negatively charged ionic micelles of the gelatin. Similar, but more complex, conditions obtain in the case of the chromium compounds, on account of the complicated hydrolytic and other internal changes.

A large number of substances giving rise to colloidal or hydrous oxides at a certain alkalinity also produce tanning of gelatin in greater or less degree.<sup>73</sup> Hardening, or tanning, by formaldehyde rests upon a different basis, probably by some type of aldol condensation, in which amino groups from the gelatin are concerned. The tanning by other organic substances, *e.g.*, *p* quinone, and quinone derivatives, by the oxidation products of pyrogallol, presumably has affinities with the tanning by tannins proper. These substances are all acidic, and their combination with gelatin can be considered as initially electrostatic neutralization of oppositely charged particles, though probably followed by more profound chemical rearrangement and combination. The presence of sulfite in organic developing solutions generally prevents any tanning by quinonoid oxidation products, but some tanning takes place in certain pyrogallol developers.

#### AFTER-PROCESSES

The principal after-processes subsequent to fixation and hardening are, for negatives, *reduction* or *intensification*; for positives, *toning*. Reduction is a photographic misnomer. The process consists in diminishing the density of the image, and is actually, chemically considered, an oxidation. It depends upon oxidizing the silver to silver ion, and removing a soluble silver salt. A colloid chemical factor in the reduction action of persulfates has been asserted by Lüppo-Cramer.<sup>74</sup> This reducer has the property of attacking the denser deposits much more rapidly than

<sup>72</sup> Cf. PAULI, Wo: Report of Symposium on "Physics and Chemistry of Colloids," Faraday Society and Department of Scientific and Industrial Research, Gt. Britain, 1921, p. 16.

<sup>73</sup> LÜPPO-CRAMER: "Kolloidchemie und Photographie," 1st ed., 1908, p. 121.

<sup>74</sup> LÜPPO-CRAMER: "Photo. Probleme," p. 95; summary article, *Phot. Korr.* (1914), 241.

the very light ones, due to lower exposures. Since it is known that silver ions catalyze the oxidizing action of persulfates, the differential action has been attributed to this.<sup>75</sup> Lüppo-Cramer, however, regards it as due to a difference in dispersity of the silver in the weakly exposed portions, compared with the strongly exposed ones, associated with a greater retention of silver halide after fixation—possibly also of thiosulfate and silver sulfide. The silver here is more protected against the persulfate. In recent papers<sup>76</sup> the writer concludes that the character of the image is fundamental, since neither the addition of acid, nor of silver ions, both of which catalyze the attack of persulfate on silver, eliminate the differential action. On the other hand, G. I. Higson<sup>77</sup> has supported the catalytic theory. The retention of adsorbed substances by the image can be demonstrated by attempting to dissolve the image completely away with chromic or nitric acids, or persulfate.<sup>78</sup> There remains a yellowish, faint image, found to consist chiefly of silver sulfide (from thiosulfate) with traces of iodide and bromide. If the plates, after hardening, are fixed in concentrated potassium bromide, scarcely any residue is visible.

Differences in the structure of the silver gel of the image, particularly according to the character of the development, also affect stages in intensification processes. In many of these the silver image is first bleached to silver halide, *e.g.*, silver chloride; a very usual reagent is mercuric chloride, when both silver chloride and mercurous chlorides form. The fine-grained, compact types of silver are much more slowly bleached than the spongy, black deposit. Very similar differences are evident in various toning processes, as used in positive processes for altering the tone of the image, since in most of these a bleaching action, *i.e.*, oxidation, precedes or initiates the actual toning. This may consist in the conversion of the silver into a colored substance, such as Prussian blue, or in the mordanting of dye to form a lake, with, *e.g.*, silver iodide, or an insoluble ferrocyanide. A number of interesting adsorption effects occur here.

<sup>75</sup> *Z. Wiss. Phot.*, **12** (1913), 311.

<sup>76</sup> *Phot. J.*, **61** (1921), 450; *Ibid.*, **62** (1922), 321.

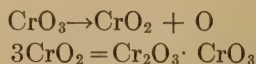
<sup>77</sup> *Phot. J.*, **62** (1922), 98.

<sup>78</sup> LÜPPO-CRAMER: "Photo. Probleme," p. 75.

## BICHROMATED COLLOIDS

Bichromated colloid processes are of fundamental importance in photomechanical reproductions, although several of them are used in photography also. All depend upon the fact that the soluble bichromates of the alkali metals and of ammonium<sup>79</sup> are reduced in the presence of organic substances. If these organic substances are biocolloids, such as gelatin, albumen, glue, or gum arabic, their properties, particularly in respect to *water*, are radically changed. This change is, in general, of the same character as the tanning or hardening already noticed in connection with the action of aluminum and chromium salts upon gelatin. This gelatin becomes insoluble in warm water, a fact taken advantage of in the carbon process. In this a gelatin layer containing a pigment is sensitized with alkaline bichromate, *e.g.*,  $(\text{NH}_4)_2 \text{Cr}_2\text{O}_7$ ; after exposure, the gelatin layer is transferred, reversed, to an intermediate support. The original lower layers, now uppermost, are dissolved out with warm water. In the bichromated fish glue or enamel process, used in half tone reproduction, a mixture of fish glue and bichromate is thinly coated on a copper or zinc plate and printed under a half tone negative. The unexposed parts between the "dots" are dissolved out with hot water, then the residual insoluble "dot" image is baked, forming an enamel or acid resist. On etching in acid or ferric chloride solution, the "dots" protect the metal below, according to their size and thickness, so that a printing block is formed. Albumen is sometimes used in conjunction with fish glue.<sup>80</sup>

The reactions involved in the photochemical process are not yet clearly understood. The reduction of the bichromate yields a brownish insoluble substance, which has been supposed to be chromium chromate:<sup>81</sup>



<sup>79</sup> Fox Talbot (1853) discovered that bichromated gelatin became insoluble in light.

<sup>80</sup> Fish glue is non-setting, and very similar to hydrolyzed glue or gelatin.

<sup>81</sup> EDER, J. M.: *Phot. Korr*; *Hdbuch J. Phot.*, **2** (1906), 177; LUMIÈRE and SEYEWETZ: *Bull. Soc. franc. Chem.*, **33** (1905), 1032, 1040; **35** (1907), 14.



However, neither the composition of the so-called chromium chromate nor of the chromium dioxide appear to have been definitely established; the substances obtained in the presence of organic matter have a variable composition, intermediate between  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_4$ . It does not seem that the tanning of gelatin in this case is quite the same as by the hydrolysis of chromium salts, but whether the oxygen released by the photochemical reaction plays a part is unknown. Lumière and Seyewetz (*loc. cit.*) established a number of empirical results. The so-called "continuing action" of light with bichromated colloids consists in the fact that, if the material is kept after a relatively brief exposure, the insolubilizing action goes on increasing in darkness. This is similar to certain other photochemical reactions in which a heterogeneous catalyst is produced by light.

## CHAPTER XXXIII

### CASEIN AND THE DAIRY INDUSTRY

By

HARPER F. ZOLLER

It is natural that the first earnest effort directed towards the unveiling of the characteristics of the constituents of milk should immediately follow the publication of Graham's<sup>1</sup> paper which demarcated colloids as one of the fundamental conditions of matter. While Hammarsten's<sup>2</sup> work on the physical relationships between the salts and proteins of milk is not now generally accepted in all its details, still it furnished the impetus for that master of technical skill, Söldner,<sup>3</sup> to proceed with one of the most painstaking and critical investigations into the dynamics of milk that has yet appeared. He appreciated that some of the constituents of milk were there in colloidal condition and he made use of the methods then available to physical chemists for their study. Thus Söldner was first to show that the calcium and magnesium salts which passed through a porcelain filter from fresh milk must be rendered soluble in the serum by means of the citrates of the alkali metals. He further reasoned that the calcium and magnesium phosphates existing in milk are held in physical suspension by the calcium caseinates and are not chemically united—a condition which we now hold to be true.

Söldner further proved that calcium and magnesium phosphates were partly precipitated from the milk serum by heating milk above body temperature, a fact of considerable importance in all dairy industries. By a judicious use of reaction indicators then available he showed that the combination of bases with casein was a progressive one, and likened a mixture of casein and sodium hydroxide, which just failed to turn phenolphthalein pink, to a mixture of monosodium phosphate and disodium phosphate with similar properties. To him casein was amphoteric.

## MILK AND ITS CONSTITUENTS

**The Constitution of Milk.**—The chief substances which compose milk, in the order of their declining amounts, are: water, lactose, fat, casein, albumin and globulin, mineral salts, together with traces of accessory materials and vitamins. Following the same order, the mineral salts consist of phosphates, citrates, potassium, calcium, chlorides, sodium, magnesium, ammonium, and traces of sulfates and bicarbonates.

Freshly secreted milk has a reaction of approximately pH 6.65, as determined electrometrically. The surface tension is lower than that of water at the same temperatures, *e.g.*, milk 0.053 and water 0.075.

Milk is a colloidal complex. Some of the most fundamental principles of colloidal behavior are excellently illustrated in milk. At its normal reaction it exists as a dense white liquid only slightly heavier than water. The fat is completely emulsified in a solution of caseinates, albuminates, globulins, and citrates. It is partially to this emulsified fat that the color of milk is due. Another factor which is important in lending whiteness to milk is the presence of finely divided calcium phosphates and other insoluble salts, which are held in suspension by the metal proteinates and citrates. When milk is left quiet, the fat globules forming the emulsion rise slowly to the surface of the milk, carrying with them their envelope of colloidal material, thus forming cream.

The colloidal envelope is made up mainly from protein material, as mentioned above. While there is probably 15 per cent of albumin and globulin present in the envelope, the salts of casein form the main body of colloidal material in milk and they will, consequently, receive the bulk of attention in this connection. This protein envelope can be readily destroyed, thereby setting the fat free. When the destruction is accomplished by acids or alkalis, the fat is in condition to be determined quantitatively, as in the Babcock and Höyberg methods. When the rupture of the protein membrane is brought about by physical or mechanical impact, butter results. If the temperature of fresh milk is slowly raised, the protein membrane becomes weak and several fat globules may run together. When milk at this temperature is

forced through a small orifice, the fat is distributed into extremely small particles and each particle of fat becomes again coated with an envelope of the protein material. If this finely dispersed menstruum is cooled, it becomes exceedingly difficult to separate the fat again. This process is called in practice "emulsification" or "homogenization." The dispersion of fat and oil in the presence of soluble protein material, in order to render the systems stable for long periods, is a procedure now made use of in a number of large industries.

At the reaction of fresh milk, casein cannot exist as such, but only as metal caseinates. The metal caseinates present in milk are chiefly of calcium and magnesium (*cf.* Söldner,<sup>3</sup> Van Slyke and Bosworth<sup>5</sup>), although there may be traces of potassium and sodium caseinates. Inasmuch as casein is a polybasic acid, it is a mixture of calcium or magnesium caseinates which exists at the reaction of milk. That which has just been said concerning casein is equally true of the albumin and the globulin present in milk. They are there in the form of their metal salts. Since they are coagulated by heat, they are very important in their action on milk products.

When milk sours as a consequence of the formation of lactic and other acids by action of bacteria on the lactose, the caseinates are transformed into free casein and the milk thickens, or clots. When the enzymes, rennin or pepsin, act on milk, a clot is also formed. These clots are somewhat similar in character. The albumin and globulin are not similarly clotted.

**Pure Casein.**—We have found that casein exists in milk in the form of its metal salts. In separating casein from milk, therefore, it will first be necessary to decompose these salts by means of a suitable acid with which the metal cations will form readily soluble compounds. When the acid is added to the milk, a heavy curd forms which engulfs some of the salts and other substances in milk. The salts which may be entrained in an undecomposed form are the calcium and magnesium phosphates. It would be necessary to leach the curd with weak acid in order to remove these compounds. The bulk of the calcium phosphate in milk is in the form of the dicalcium phosphate and, unless this is converted into monocalcium phosphate, it will not become soluble. The method of Hammarsten<sup>2</sup> for producing pure casein



depended upon the precipitation from diluted skim milk with acetic acid, washing the curd, redissolving in the least quantity of alkali necessary to make a solution, and then reprecipitating this solution with acetic acid, washing, and drying with alcohol and ether. This casein was contaminated with traces of dicalcium phosphate and possibly some albumin.

Van Slyke and Bosworth<sup>5</sup> sought to improve upon Hammarsten's method by the substitution of distilled water and ammonium hydroxide in place of sodium hydroxide. They also suggested the use of ammonium oxalate and subsequent centrifugation to remove the calcium before washing. Van Slyke and Baker,<sup>6</sup> using the limits determined by Michaelis and Pechstein,<sup>7</sup> obtained a calcium-free casein in a very different manner. Dilute acid was added to diluted skim milk very slowly while the entire mass was vigorously stirred. The reaction of the milk and acid was brought to the isoelectric point of casein, pH 4.6. After stirring at this reaction for a time sufficient to transform all of the phosphates into a soluble form, the casein was filtered, washed, and dried.

Clark and his co-workers<sup>8</sup> found that in the preparation of commercial casein from pure skim milk and hydrochloric acid, by means of the indicator control of hydrogen ion concentration in the vat, the casein could be produced practically calcium-free by simply washing the finely divided grained curd with distilled water adjusted to pH 4.6. Zoller<sup>9</sup> called attention to the necessity of knowing the history of the milk from which the casein was made; otherwise if the skim milk had been pasteurized or otherwise strongly heated there would be amounts of coagulated proteins other than casein (albumin and globulin) and larger quantities of alkaline earth phosphates, which could be only partly removed in the precipitation process. Northrop<sup>10</sup> recently called attention to a mode of precipitating casein in which he claims that denaturation of the casein by acid is avoided. He precipitates casein from skim milk with hydrochloric acid without taking precautions against adding too much, and, after a preliminary washing of the curd with water to remove the salts, he plunges the casein curd into water and adds an excess of acid until pH 2.5 to 3.0 is reached. The casein is, consequently, transformed into casein chloride, which exists as a translucent

solution. After filtering, the solution is then adjusted to pH 4.7 with sodium hydroxide and the curd thoroughly washed. After going over the process carefully in the laboratory, it could not be seen where the question of denaturation by acid was avoided in his process. It is believed that the observations on the cloudy solutions of casein in alkali are incorrectly interpreted, since both coagulated albumin and precipitated alkaline earth salts are extremely difficult to remove by the single precipitation process of Van Slyke and Baker.<sup>6</sup>

L. Van Slyke and Carpenter<sup>11</sup> have recently developed the use of electrolysis for the purpose of freeing the casein from its salts. They claim that a very superb and pure form of casein can be produced by this process. Analytical data substantiate their claims.

The writer has succeeded in preparing a pure casein in fairly large amounts by the following method: Fresh, unheated skim milk is diluted with distilled water in the proportion of 1 volume of skim milk to 2 volumes of water. It is warmed to 30°. A mixture of pure 5 per cent hydrochloric acid and 5 per cent citric acid is slowly added to the milk beneath the surface with rapid stirring until pH 4.6 is reached. After stirring for 10 minutes longer the casein is centrifuged from the liquor in a small basket centrifuge. It is resuspended in distilled water adjusted to pH 4.6, stirred, and finally centrifuged three more times. The finely divided curd is now suspended in distilled water and hydrochloric acid added slowly until the final pH is 3.0. After thorough solution is effected, the casein hydrochloride is precipitated with ammonium hydroxide at pH 4.6, and is again thoroughly washed with distilled water at pH 4.6, centrifuged, and subsequently dried with pure acetone or alcohol. The sodium, potassium, or ammonium caseinate made from this casein is water-clear, and gives no test for calcium by spectroscopic analysis of the ash. Careful analysis for phosphorus and sulfur shows 0.78 and 0.808 per cent respectively.

Pure casein is a white amorphous powder. It is with difficulty wetted by water. That it is slightly soluble in water has been shown by Robertson,<sup>12</sup> and more recently by Cohn.<sup>13</sup> Its slight solubility is attested by the fact that it will release CO<sub>2</sub> from carbonates and SO<sub>2</sub> from sulfites when the powdered casein

is added to an aqueous solution of carbonate or sulfite. Particles of the dry casein, when rubbed by friction, become highly electrified. The specific gravity of pure casein is 1.257. It is not hygroscopic in its pure state, but if it contains much ash it becomes a good meter for humidity (Zoller<sup>8</sup>).

When casein is suspended in water and the mass is heated slowly to 80 to 90°, the casein begins to imbibe water rapidly, and becomes plastic. In this form it can be stretched or molded into any form desired. Upon cooling, it again becomes hard and resembles the consistency of horn. In this property of absorbing water when heated it is similar to gelatin and other proteins. It differs from some of them, however, in resisting coagulation by heat at temperatures up to 100°.

From a chemical standpoint, casein is a phosphoprotein, since in its purest form it contains about 0.8 per cent of phosphorus. It also contains about 0.8 per cent of sulfur. Casein contains about 15.6 per cent of nitrogen, 5.5 per cent of which is in the form of free amino groups. It is largely due to the sulfur, phosphorus, and amino nitrogen that casein owes its amphoteric character. Measurement of the combining power of casein with bases by Robertson,<sup>12</sup> Laqueur and Sackur,<sup>14</sup> Yamakami,<sup>15</sup> and others indicates that the molecular weight of the casein entity is some multiple of 2,100 to 2,400.

Moisture-free casein is dissolved by anhydrous formic and acetic acids to form clear mucilaginous solutions. The casein can be recovered from this solution by careful dilution with water and reprecipitation by alkalies.

Cohn and Hendry<sup>13</sup> calculated the acid dissociation constant for casein and arrived at a solubility product constant of  $2.2 \times 10^{-12}$  g. of casein per liter at 23°.

**Salts of Casein.**—We have said that casein is amphoteric, that it is capable of forming salts with either acids or bases. In aqueous solution these salts are ionizable, and the type of ions dissociated depends upon the hydrogen ion concentration of the solution. Hardy<sup>16</sup> demonstrated that protein bodies in solution carried an electrical current and migrated in an electrical field towards the poles furnishing the current. The direction of migration of the protein particles was determined by the acid-base reaction of the medium. When the solution was acid, the



protein moved from the anode to the cathode, and in the opposite direction when it was alkaline. Hardy further believed that there must be a point of reaction in the medium at which no motion of the protein particles could be detected. This point he termed the "isoelectric point," because the electrical charges on the protein material must be equal in number, otherwise, should there be more charges of one sign than the other, the protein would be attracted towards the electrode bearing the opposite charge. Since this demonstration of Hardy in 1900 there have been numerous investigations into the isoelectric phenomena of organic compounds. One is safe in remarking that all amphoteric substances possess isoelectric states. Casein is isoelectric when it is combined with neither acid nor base. Michaelis and Pechstein<sup>7</sup> found this to be at a hydrogen ion concentration of  $2.4 \times 10^{-5}$ , or pH 4.6.

Casein differs from most of the proteins in being nearly insoluble at its isoelectric point. This fact, however, renders the preparation of pure casein a comparatively easy operation. There is a sufficient ionization of casein, even at its isoelectric point, so that salt formation may proceed quite rapidly. When pure casein is suspended in distilled water and a small amount of dilute alkali is added, the outside of the protein particles become immediately coated with a film of alkali caseinate. This caseinate slowly dissolves or disperses in the medium and more caseinate is formed. This process continues until an equilibrium is established between casein and alkali, provided, of course, that the quantity of alkali added was not sufficient to saturate the protein. A similar process takes place with an acid like hydrochloric, acetic, and lactic. The alkali caseinates are all soluble in water. Casein chloride, casein acetate, and casein lactate are readily soluble in water, while casein trichloracetate, casein sulfate, and casein oxalate are difficultly soluble (Loeb<sup>17</sup>). The casein salts of the alkaline earths, such as calcium, magnesium, barium, etc., are less soluble than the alkali salts. Casein combined with small amounts of calcium, the acid calcium caseinates, dissolves in water to form a milky solution, but, as the content of calcium is increased, the salt becomes less and less soluble. It likewise becomes less stable towards heat.



Robertson<sup>12</sup> has determined in a very beautiful fashion the combining capacity of casein for bases. By means of the gas chain he measured electrometrically the quantity of potassium hydroxide in equivalents held by casein up to its saturation point. The results are given as follows:

Salt 1 containing  $11.4 \times 10^{-5}$  equivalents of KOH per 1 g. casein.

Salt 2 containing  $22.8 \times 10^{-5}$  equivalents of KOH per 1 g. casein.

Salt 3 containing  $45.6 \times 10^{-5}$  equivalents of KOH per 1 g. casein.

Salt 4 containing  $91.2 \times 10^{-5}$  equivalents of KOH per 1 g. casein.

Salt 5 containing  $182.4 \times 10^{-5}$  equivalents of KOH per 1 g. casein.

The table shows that 16 molecules of a monacid base, such as sodium hydroxide, may combine with 1 molecule of casein. When  $182.4 \times 10^{-5}$  equivalents of a base is combined with 1 g. of casein, a condition arises which Robertson found when an excess of base was present: there must be either a direct union of 16 mols of the base with 16  $-\text{CONH}-$  groups in the protein molecule, or else the sulfur and phosphorus within the molecule are claiming their share of the base. Zoller<sup>18</sup> showed, while studying the viscosities of sodium caseinates, that when casein had combined with  $180 \times 10^{-5}$  equivalents of base per 1 g. of casein the reaction of the solution was so alkaline that not only ammonia but also sulfur and phosphorus were broken loose from the casein molecule. His data for casein solutions containing 8 per cent of protein revealed a maximum viscosity for caseinates at pH 9.0 to 9.2 and a combination with base at this point of approximately  $90 \times 10^{-5}$  equivalents per 1 g. of casein. Robertson noted that the casein solution was red to phenolphthalein when 1 g. held  $90 \times 10^{-5}$  equivalents.<sup>12</sup> Loeb,<sup>17</sup> on the other hand, found that the maximum viscosity of sodium caseinate appeared in a 1 per cent solution of the protein at approximately pH 11.5. This is in the same region of pH in which the casein molecule has united with 16 mols of the monacid base, according to the titration curves of Robertson, Zoller, and Loeb. In

view of the rapid hydrolysis of casein at pH greater than 10, we are incorrect in accepting that the true casein molecule can combine with more than  $90 \times 10^{-5}$  equivalents of base per gram without undergoing external decompositions. Sackur<sup>19</sup> found that the viscosities of alkali caseinates follow the Arrhenius-

Euler formula  $\frac{\eta}{\eta_0} = A^n$ , when they contain about  $80 \times 10^{-5}$  equivalents of base per gram. This is at neutrality to phenolphthalein. In the above formula  $\eta$  is the viscosity of the solution,  $\eta_0$  is the viscosity of the solvent,  $n$  is the concentration of the solute, and  $A$  is a constant which is dependent upon the temperature and nature of the solute.

Loeb<sup>17</sup> is led to believe that the viscosity of solutions of proteins is primarily a function of the relative volume occupied by the protein in solution. The volume of the protein particles is determined by the hydrogen ion concentration of the solution, the valency of the ions taking part in the equilibrium and the sign of the electrical charge on the ions. In the equation for the Donnan equilibrium existing between two sets of media on opposite sides of a membrane, only the sign of charge and the valency of the ions are concerned under a given set of conditions. Loeb found that the viscosity of casein chloride, acetate, phosphate, etc., were at their maximum at about pH 3.0. Naturally, the magnitude of the viscosity decreases to a minimum at the isoelectric point of casein, for it is at this point that casein is scarcely ionized, or, at least, is at its minimum of ionization.

Robertson<sup>12</sup> showed that both alkali caseinates and casein acid salts (casein chloride) obey in part the Oswald dilution law as regards the specific conductivity of their dilute solutions. The specific conductivity of the monacid basic caseinates is twice as great as that of the diacid basic caseinates in dilute solutions. This finding is in harmony with Pauli's<sup>20</sup> theory of the hydration of protein ions. Loeb<sup>17</sup> has since measured the conductivity (electrical) of casein salts in 1 per cent solution at definite pH and finds that the results are not in agreement with those demanded by the hydration theory.

The osmotic pressures exhibited by salts of casein in aqueous solution are in parallel agreement with the viscosities exhibited by these same solutions (Loeb<sup>17</sup>).

The amount of ethyl alcohol required to precipitate the casein salt of any monovalent anion or cation is considerably larger than the amount required to precipitate the casein salt of a divalent or polyvalent anion or cation, when such salts are in aqueous solution. This is in accord with the majority of the physical properties of casein solutions. Thus Robertson notes:<sup>12</sup>

The degree of dissociation of the caseinate in the solutions containing 60 per cent and less of alcohol is evidently but little affected by the percentage of alcohol in the solvent, the major part of the effect of the alcohol upon the conductivity being attributable to the decreased mobility of the caseinate ions.

The molecular condition of the casein in alcohol-water solutions seems to remain unchanged in concentrations of alcohol up to about 70 per cent. The Ostwald dilution law holds very closely up to this point. Above this point, however, the dissociation of the caseinate is seriously affected. When this critical point is reached, the quantity of salts which are necessary to precipitate the casein salt from the alcohol-water solution changes materially. Robertson believed that polymerization of the caseinate ion resulted near this critical concentration of alcohol, and he has strong evidence for concluding that the precipitation is brought about by dehydration of the protein. Loeb<sup>17</sup> states:

It is possible to show that when the amount of alcohol exceeded the critical limit, the forces guaranteeing the stability of the solution of gelatin in alcohol-water mixtures are the forces resulting from a Donnan equilibrium.

His demonstration consisted in proving that the effective ion in producing the precipitation now has an electrical charge of opposite sign to that of the colloidal particle, when this critical concentration is reached. According to Loeb, the valency is the deciding factor in the precipitation limits at the critical point when the sign of the charge on the precipitating ion is opposite to that of the protein ion. Whichever view one may come to share, it is sufficient to remember that the salts of casein conduct themselves, in dilute solution, according to the generally accepted laws of inorganic chemistry.

The minimum quantity of a monobasic acid necessary to hold casein in solution is  $32 \times 10^{-5}$  equivalents per gram, while the minimum amount of any monacid base required to dissolve casein is  $11 \times 10^{-5}$  equivalents. For calcium hydroxide,  $22 \times 10^{-5}$

equivalents are required to produce a soluble compound. Robertson<sup>12</sup> deduces the electrochemical equivalent of casein to be  $2,336 \pm 183$ . Cohn and Hendry<sup>19</sup> find that 2,100 is the combining weight, as shown by the quantity of casein combining with 1 mol of sodium hydroxide.

**Hydrolysis of Caseinates in Aqueous Solution.**—Zoller<sup>18</sup> showed that caseinates begin to suffer alkaline hydrolysis at about pH 10 and the hydrolysis continues as the alkalinity increases. It is important, therefore, in the preparation of caseinates and in the determination of the combining capacity of casein with bases, that this point be not overstepped.

On the acid side of the isoelectric point the maxima of the physical properties appear at about pH 3.0, and they immediately drop to a small value. Acid hydrolysis must of necessity commence somewhere in the neighborhood of this drop or flattening of the curve. There is no record of it ever having been determined for casein.

Solutions of casein are reported to be stable towards heat. In fact, most of the alkali caseinates can be heated to boiling without any apparent change in their physical appearance. We know, however, that if we reprecipitate casein from these solutions which have been boiled, it has different properties. It holds more water at the isoelectric point and is slower to redissolve in alkali or acid. It has become denatured. The writer<sup>24</sup> found that when solutions of pure casein in carbonate-free alkali were adjusted to different pH by means of the casein and sodium hydroxide, these solutions could be coagulated by heating to 135° in sealed glass tubes. The precipitate or curd, when dried, resembled casein in that it was dissolved by alkalies and acids. That it was not casein was shown by the fact that the isoelectric point was lower than that for casein (pH 3.8 to 4.0). The term *β casein* is suggested for this form which is precipitated from casein solutions at high temperatures.

Solutions of alkaline earth caseinates behave like the above when subjected to similar heat treatment in sealed spaces. This fact must have an important bearing in certain industrial processes where milk is heated to autoclaving temperatures.

**The Coagulation and Precipitation of Caseinates.**—Any of the common acids will release casein from the caseinates. Even



carbon dioxide under pressure brings about the coagulation. Each acid will exert a special influence upon the character of the curd or coagulum. When strong acids are used to precipitate casein from caseinates it is absolutely essential that very small quantities of acid in diluted form be added to the solution of casein, and, further, that the dilute caseinate solution be thoroughly stirred so as to bring the acid in contact with all of the solution in order that local hydrolysis may be avoided. In the case of treating milk with strong acids, this same feature should be utilized, although milk contains many polyacid salts and other proteins which act as buffer material against the strongly ionized acids. The pure solutions of caseinates, on the other hand, are weakly buffered, except by the polyacid casein itself, and form huge clumps of curd, when the acid is added, which engulf much undecomposed caseinate unless the precautions mentioned above are taken.

Less strongly ionized acids, such as lactic, acetic, citric, etc., the ionization constants of which are close to the isoelectric point of casein ( $2.4 \times 10^{-5}$ ), are more suited for the precipitation of casein from its solutions, since there is less chance for overstepping the isoelectric point with the consequent formation of casein acid compounds. The nature of the resulting curd when the different acids are used in the precipitation is characteristic of the fact that each anion exerts a separate influence upon the physical texture, depending partly upon the valency and partly upon other factors not definitely developed. Loeb<sup>19</sup> explains the difference in the action of sulfuric acid on the texture of freshly precipitated curd from milk, described by Zoller,<sup>9</sup> by assuming that at a constant pH, such as the isoelectric point of casein, sulfuric acid dissociates as a divalent anion because of its great strength as an acid at this point, whereas other polybasic acids, such as citric, phosphoric, and tartaric, behave like monobasic acids at this reaction and dissociate a monovalent ion. Sulfuric acid is an entirely unsatisfactory acid to use in the isolation of casein, either from milk or from simple caseinates, because the curd is always very soft and dispersed like a curd which had imbibed excessive quantities of water.

When water solutions of egg albumin or milk albumin are heated, they are said to coagulate as the temperature approaches

65° in case of the former, and 75° in case of the latter. Pauli and his students consider that this form of heat coagulation is a dehydration process, and similar in all respects to the coagulation of the albumins by salts and alcohol. Robertson believes that the dehydration is accomplished by a type of polymerization of the end  $\text{-NH}_2$  groups and adjacent  $\text{-COOH}$  groups in the same molecule through the action of heat and splitting off of water. Chick and Martin reasoned that the heat coagulation was a process of hydration, because thoroughly dry protein, when heated to high temperatures, does not lose its solubility in water.

Casein solutions are not affected by heat in the same manner as the albumins. Pure casein is only very slightly soluble, so that we do not know what the effect of heat on a pure casein solution would be. On the other hand, both alkali albuminates and caseinates are soluble, and we do know that alkali albuminates coagulate readily by heat, whereas alkali caseinates do not coagulate unless considerably higher temperatures are used. The quality of the casein is affected, however, as is evidenced by the color, solubility, and physical behavior of the product.  $\beta$  casein is considered by Zoller<sup>24</sup> to be a denatured form of normal casein.

In the precipitation of casein from solution and from milk by the addition of metallic salts, we are forced to consider at least two separate reactions. If we hold that the coagulation of proteins from solution by means of magnesium or ammonium sulfate is an example of dehydration, as Pauli believed, then this reaction is one of those to be considered. The second type of reaction is illustrated by such salts as aluminum or copper sulfate. When either of these salts are added to a pure caseinate or to milk, a coagulation is immediately produced. The cause or causes of this coagulation are twofold. We might consider that a simple case of dehydration resulted in the coagulation, but we are forced to regard the reaction of the coagulation from the standpoint of the hydrogen ion concentration. Both the copper and the aluminum sulfate are strongly acid, and, upon examination of the completely coagulated solution, we find that the reaction is approximately at the isoelectric point of casein (pH 4.6).

In alkaline solution casein behaves as any other alkali salt behaves, and because of the multiple basicity of the acid casein,

the number of salts formed with a single alkali is large, and is governed by the alkalinity of the solution. If a soluble metallic salt is added to a soluble caseinate, a direct double decomposition reaction proceeds at first to form either a soluble or an insoluble caseinate, or, in case the metallic salt dissociates many hydrogen ions, a quantity of free casein may be formed.

When small quantities of soluble calcium salts are added to milk or caseinate solutions, coagulation immediately occurs. The product is generally an insoluble calcium caseinate, unless the calcium salt solution had a pH near to the isoelectric point of casein, in which case the coagulum would contain some free casein. This reaction is considered to be of great importance in the coagulation of milk by both rennin and pepsin.

The enzyme coagulation of casein cannot be brought about in true form except in the presence of calcium ions. Both rennin and pepsin produce a similar coagulum, and in a similar manner under like conditions. Pure sodium caseinate solutions do not form a clot with rennin or pepsin when held under the optimum temperature conditions. When some soluble calcium salt is added to the caseinate solution containing the enzyme, immediate clotting takes place. In the light of the information given in the preceding paragraph regarding the effect of calcium salts on milk and caseinates, it may be incorrect to assume that there had been some action on the sodium caseinate by the enzyme. Fuld,<sup>25</sup> Madsen,<sup>26</sup> and others have shown that in the coagulation of milk by rennin the velocity of coagulation is proportional to the concentration of the enzyme. It was also shown that the law of Schütze, which states that the velocity is proportional to the square root of the fermenting mass, holds very true for this enzyme coagulation.<sup>27</sup>

In the enzymic hydrolysis of casein, Bosworth<sup>28</sup> holds that the paracasein is first formed and that it is the combination of calcium with the paracasein which produces the clot. Bosworth further shows that the minimal combining power of paracasein for bases is just twice as large as for pure casein. Of the true nature of the enzyme coagulation, we know very little. The nature of the milk clot is vastly important for the dairy industry from the standpoint of cheese making. Pasteurized milk forms a different type of curd than unheated milk; the curd is softer,



holds more water, is more difficult to handle, and is comparable in differences to the curd described by Zoller,<sup>9</sup> which is precipitated by acids from pasteurized milk. While the pasteurization has caused a partial precipitation of calcium ions in the form of calcium phosphate within the milk, thus retarding the rennin action, it has also caused a partial denaturation of the colloidal protein.

**Protective Colloidal Property of Casein Solutions.**—An important property of colloids from the applied standpoint is their tendency, when in solution, to prevent or retard other substances from being thrown out of solution. Zsigmondy<sup>29</sup> found that it required a certain amount of salt to precipitate a dispersion of colloidal gold, but that when gelatin was present it required a large amount to flocculate it. A soluble caseinate was discovered to be as efficacious as gelatin in this respect, and either one was 20 times as strong a protective agent as gum arabic. The protective action is believed to be brought about by the colloidal agent forming an envelope of protective material around the particles which are to be protected. Thus, on the finely dispersed fat globules in milk we have a protective coating of the milk proteins enveloping them and tending to prevent them from coalescing. The fat particles with their cloak of protein material bear an electrical charge, the sign of which is the sign of the charge on the protein ion. If one wishes to destroy this protective envelope, it is necessary to neutralize its electrical charge by the addition of some agent of unlike electrical charge. Another means of destroying the protective envelope is to bring about the denaturation of the envelope material through some physical agency, such as heat, excessive pressures, or freezing. In the freezing of protein material, there is a certain amount of dehydration and redistribution of water between the solid and liquid phase which effects a typical denaturation of the colloid.

The protective action of caseinates decreases markedly to zero as the reaction of the solution passes through the isoelectric point and then increases as the casein again goes into solution as a cation on the acid side of the isoelectric point. While it is shown that gelatin possesses a lower protective action at its isoelectric point (pH 4.7), this value never drops to zero because of the solubility of isoelectric gelatin.



**Casein Addition Compounds and Decomposition Products of Colloidal Nature.**—If a dilute formaldehyde solution is added to a solution of sodium or other caseinate a heavy coagulation ensues. Other aldehydes behave similarly with caseinates. The formaldehyde is supposed to condense with the  $-NH_2$  groups in the casein molecule forming methylene linkages with the subsequent elimination of one molecule of water for each molecule of formaldehyde added. When formaldehyde-casein complex is purified it is found to behave somewhat like gluten, forming a plastic mass which when heated can be moulded into any shape desired. As it hardens it becomes bone-like and can be sawed and polished, in which form it is known as *galolith*.

If we treat casein acetate or other acid salt with nitrous acid the amino groups in the casein molecule are again attacked, but this time there is an elimination of free nitrogen and water while an hydroxyl group is supposed to take the place formerly held by the amino group. Lewis<sup>30</sup> has studied this product somewhat and shows that the deaminized casein forms a gelatinous mass when it is dispersed with ammonium hydroxide in water.

Casein which has been allowed to react with a 25 per cent solution of sodium hydroxide at body temperature for several hours, evolves considerable ammonia (Dakin<sup>22</sup>) and looses bound sulfur and phosphorus (Maynard;<sup>23</sup> Zoller<sup>9</sup>). When the alkaline solution is diluted and treated with dilute acid a soft, slimy curd forms which will redissolve in alkalis. The dried purified product now contains no sulfur or phosphorus. Dakin has asserted that the amino acids which can be hydrolyzed from it are all inactive towards polarized light.

Caseinates combine readily with the halogens to form substitution and addition compounds. They are all soluble in alkalis and acids, and possess isoelectric points not widely separated from that of pure casein. Zoller<sup>21</sup> has shown that when sodium caseinate is treated with sodium hypochlorite at reactions between pH 6.0 and pH 9.0 a chlorocasein is formed which precipitates at a point slightly lower than pH 4.6. The curd is similar to casein except that it is pink in color and dries to a deep flesh tint. The chlorocasein when dissolved in alkali possesses a greater viscosity than ordinary caseinates. It shows a higher gold number than casein.

## IMPORTANCE OF COLLOIDS IN THE DAIRY INDUSTRY

**Pasteurization and Market Milk.**—Ordinary cows' milk contains about 0.75 per cent of coagulable (by heat) proteins, mainly albumin and globulin. These proteins exert a protective effect upon the size and texture of the casein curd whenever the milk comes in contact with acid, such as souring caused by acid-forming bacteria or the gastric juice of the stomach. If the content of these proteins is increased, the curd becomes much softer and the curd grains less regular in form. In woman's milk and in the colostrum the heat-coagulable proteins bear a higher ratio to the casein, consequently the curd from these milks is very soft and difficult to form.

Hawk<sup>39</sup> showed very clearly that pasteurized milk clotted into finer and softer curd in the stomach of the individual than did unpasteurized milk. Zoller<sup>24</sup> showed that temperatures of pasteurization caused a certain amount of precipitation of alkaline earth phosphates within the milk, and that this may have been in part responsible for the condition of the curd which is precipitated by acids in the commercial preparation of casein from pasteurized milk.

Herter,<sup>33</sup> Alexander,<sup>34</sup> and Downey<sup>35</sup> have shown the influence of added gelatin on the type of curd formation in milk when the latter comes in contact with acids. Experimental feeding tests show that milk containing gelatin is more rapidly and completely digested by the infant. The gelatin, because it is soluble at the isoelectric point of casein, protects the particles of isoelectric casein from flocculating into large curds. Although sodium caseinate and gelatin possess approximately the same gold number, the one may become the protector of the other when the other assumes a different physical state.

**Evaporated and Condensed Milk Products.**—The curdling of plain evaporated milk in the can immediately following sterilization is an illustration of a complex colloidal condition which is a financial annoyance to the dairy manufacturer. The evaporation of milk in the vacuum pan usually takes place at a temperature below the optimum coagulation temperature for the heat-coagulable proteins in the milk. Thus, when the evaporated milk is placed in the cans, there would have been only a small

quantity of the alkaline earth phosphates precipitated during the concentrating process as well as a slight denaturization of the entire protein matter. When this milk is sterilized, it coagulates readily without standing the degree of heat necessary to kill the organisms of spoilage. It was found that, by heating the whole milk above the coagulating point of the heat-coagulable proteins in order that the latter would be entirely coagulated before evaporating (above 82°), the evaporated product would then stand more heat while sterilizing in the can than when the milk had not been preheated to the high temperatures. Hart and Sommer<sup>36</sup> made a quantitative study of the calcium, magnesium, phosphate, and citrate content of those evaporated milks which did and those which did not coagulate during sterilization. They showed that when the milk contained either an excess of calcium and magnesium or of citrates and phosphates that the calcium caseinate within the milk became unstable and coagulated under the temperature conditions necessary to sterilize. They further found that acidity played no greatly important part, unless in excess. Zoller,<sup>24</sup> following an independent study with solutions of pure milk salts, showed the retarding action of citrates on the precipitation of calcium phosphate by heat. By increasing the citrate content, more calcium was held in solution, and, consequently, the pH of the solution did not decrease in the manner that it would have done if the calcium had been precipitated in the form of the phosphate. As a result of this study, Zoller predicted that salt equilibrium in evaporated milk could be made more stable by the addition of sodium citrate or sodium phosphate to the milk, the former by holding the calcium in solution, and thus reducing the drop in pH during sterilization, and the latter by throwing part of the calcium out of solution as the phosphate, but doing so without the accompanying drop in pH during sterilization. This was shown to be the case in the experiments recently reported by Sommer.<sup>37</sup> Zoller<sup>24</sup> further showed that when solutions of caseinates were heated to sterilizing temperatures there was a precipitation of  $\beta$  casein in consequence of the great drop in pH during the heat treatment.

In the evaporation of milk with cane sugar to produce sweetened condensed milk, after ignoring the questions of microbiology, we find that the cane sugar exerts a profound effect upon the



viscosity and physical condition of the product. There are two factors involved. The first is the influence of sucrose on the swelling of hydrated proteins. The second is the tendency of sucrose and lactose to combine with calcium salts to form compounds of which the commercial article *viscogen* (calcium succinate) is an example.

**Dried Milk Products.**—Spray processes which utilize both evaporation and pressure spray exert a double denaturing influence on the resulting product. The method which simply sprays the raw milk under low pressure in the drying blast certainly yields a product in which the proteins and unstable salts are in a better physical condition for redispersion. Palmer and Dahle<sup>38</sup> reported some work which has shed considerable light on a few of the physical properties possessed by the different types of powdered milk. Holm's<sup>39</sup> study of the hygroscopicity of milk powders has furnished a basis for the partial regulation of their keeping qualities.

There are two phases of the problem not yet clearly understood. The problem of redispersion in water is a time reaction and its influence on the palatability of the resulting milk is important. Also, the small change in reaction which exists between "remade" milk and the fresh milk from which the powder was made should be studied. This slight change in reaction which is brought about by partial precipitation of some of the milk salts and denaturation of the proteins affects in no small degree the subsequent redispersion of the milk powder and the flavor of the "remade" milk. The salt content of the water which is to be used for redispersion of the powder and its influence on the resulting pH of the milk must be carefully controlled.

**Whipping Cream.**—To give a satisfactory whip, the fat must be thoroughly chilled or solidified. There must also be a sufficiency of protein present to furnish the foam interfacial films for incorporation of the air. When these conditions are met, a stiff, smooth product will result which will not flocculate when added to hot tea. On the other hand, if we take exactly the same cream and pass it through an homogenizer which only breaks the fat into small globules, and perhaps coagulates some of the protein material, the cream will not whip. The explanation of the reason for the lost whip lies in the fact that the break-



ing up of the fat into smaller globules yielding a total increase in surface has reduced the amount of protein material available for foam in solution. Most of the protein is now required for the colloidal film around the fat. If we add soluble caseinate to the homogenized cream we will in a large measure restore the whipping quality. Homogenized cream is likely to flocculate when added to hot tea or coffee.

**Butter Making.**—That which has been said about the difficulty of whipping homogenized cream also applies to the churning of homogenized cream. It is practically impossible to churn homogenized cream after the pressure to which the cream is subjected exceeds 500 lb. We attribute this difficulty also to the reduction of the protein available for foam. This is caused by the competing action of the finely divided fat for the protein to form the surface film. Rahn<sup>40</sup> has proposed the theory that, in order for proper churning, a foam must exist or be produced by the mechanical agitation. This foam consists of a protein and fat lattice, but the fat is constantly loosing its protein film to the foam lattice which surrounds the enclosed air. Thus the fat constantly looses protein and finally coalesces with the neighboring globules and the butter is said to “break.” Coincidentally with the formation of the butter, the foam disappears. Van Dam<sup>41</sup> argues that a thermoequilibrium must exist in the butter fat before butter can be produced, and the resulting buttermilk possesses a low fat content.

It would be interesting to apply Rahn’s theory to the churning of homogenized cream, by increasing the milk protein content of the cream through the addition of evaporated skim milk or a soluble caseinate. This would furnish the necessary reduction in surface tension and at the same time offer the soluble protein for the formation of the foam membranes.

**Cheese Making.**—Perhaps the greatest single problem in the cheese industry is that concerned with the production of skim milk cheese, wherein the final product is composed almost entirely of protein and water. The higher the content of protein in cheese the harder and more inedible it becomes. Proper methods for processing the protein material must be developed so that there will exist a different distribution of water in the finished product. Perhaps a partial predigestion of the curd while it is

still in contact with the whey and coagulating enzymes would aid in the solution of this problem.

In the last few years a practical application of the property of casein to become plastic at high temperatures has been made in the cheese industry. The ripened cheese is heated with proper stirring to the point at which it becomes stringy. It is then worked into a thick paste at pasteurizing temperature and molded into special forms or filled into cans for merchandising. The advantage of certain salts in rendering the cheese curd more plastic is well known in this connection.

It should not be necessary to call attention to the desirability of placing on a more scientific foundation the formation of the curd by the coagulating enzymes. This process, as customarily practiced in the vat, is at fault in that the end points are a matter of rule-of-thumb rather than definite measurement. The acidity is determined by the old method of titration and does not show the true reaction necessary for absolute duplication of results. Variations in the protein and salt content of the milk affect the value of the titration figures, whereas the optimum acidity for the proper texture of the curd is not truly indicated by using the same titration figures day after day.

Whey cheese production depends upon the utilization of the whey from swiss and cheddar cheese manufacture for the source of the curd. Whey from cheese contains essentially the heat-coagulable proteins of milk—albumin and globulin. Okuda and Zoller<sup>42</sup> have worked out the successful limits for the economical production of the curd for this product. They found that the largest yield was obtained by coagulating the whey adjusted to pH 4.5 and suggested that this point must represent the isoelectric point for the major protein remaining in the whey. They further showed that these same limits would serve for the production of "protein-free milk" of a lower protein content than has hitherto been produced for commercial feeding experiments.

**Ice Cream Manufacture.**—The use of gelatin in ice cream for the reduction of iciness has been stimulated largely through the efforts of Alexander.<sup>34</sup> Zoller pointed out<sup>43</sup> that gelatin caused the cream to freeze quicker when the mix was being frozen in the power freezer. Gelatin acted like sand and other abrasives in preventing the supercooling of the mix, and by this rapid

and steady freezing caused the ice crystals to exist in finer condition. The same effect could be produced by increasing the protein content of the mix through the use of other proteins or by the use of glucose. In every case where supercooling was prevented, the product was very smooth and free from noticeable ice crystals.

The ability of the ice cream mix to enmesh air and to hold it while it is frozen is a factor of importance to the manufacturer. Many have conceived that viscosity is of importance in this direction. We cannot, however, hold that such is the case, because we may increase the viscosity of the mix to a jelly with gelatin without increasing the yield of the mix. On the other hand, the writer has found that a very thin mix will have an overrun or yield capacity twice as great as the high viscosity mix and, if correctly hardened and stored for serving, will hold the enmeshed air without frothing when melting down in the dish. The writer believes that the chief factor (physical) in maintaining the proper yield with the ice cream mix is that of *adhesivity*. The adhesivity of the ice cream mix may be increased by the addition of more milk protein to the mix or of other protein material which does not set to a jelly as does gelatin. As the fat content of the ice cream mix is raised, there must be a corresponding increase in the protein to act as the film-forming material for the finely divided fat when the mix is homogenized, and at the same time there must be a sufficiency present to form the membrane around the enmeshed air during the freezing process.

Much attention has been given by ice cream men to commercial improvers. These are largely diluted forms of rennin and pepsin powders. When they are added to the ice cream mix they cause a thickening because of the action of the enzyme on the caseinate in the milk products used. This thickening is a result of the clotting of the casein.

A factor of no small importance to the ice cream manufacturer is the lactose crystallization in the frozen ice cream, generally known as sandiness. Zoller and Williams<sup>44</sup> have given photographic evidence of the existence of lactose crystals in ice cream which was said to be sandy. They set 10.5 to 11 per cent of normal milk solids not fat as the safe limit to which these solids could be used in a 10 per cent fat ice cream without fear of the

development of sandiness. Zoller<sup>44</sup> found also that gelatin helped rather than prevented the formation of lactose crystals in an ice cream mix containing more than the safe limit of lactose. Figure 1 shows flasks containing the same content of lactose and varying concentrations of gelatin in the same weight of solution. As the gelatin content increases, more lactose crystallizes out.

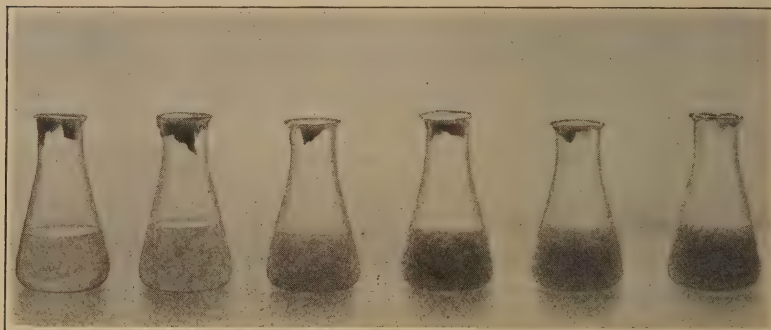


FIG. 1.—Showing influence of the concentration of protein material on the crystallization of lactose from water solution. The flasks all contain the same concentration of lactose (50 per cent). From left to right the concentration of gelatin in each flask is as follows: 0.5, 1.0, 2.0, 4.0, 8.0 and 16.0 per cent. The solutions were heated to 80°, cooled to 20° and had set at 20° for 36 hrs. when the photograph was taken.

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## CHAPTER XXXIV

### SANITATION

#### A Specific Application of Colloid Chemistry to the Development of the Activated Sludge Process of Sewage Disposal at Milwaukee

By

JOHN ARTHUR WILSON

The whole field of sanitation offers almost virgin soil for the application of colloid chemistry. Leaders in the sanitary world have only very recently come to appreciate that in a knowledge of colloidal behavior lies the means for great strides in the development of methods of sanitation. Although many promising papers have appeared dealing with the application of colloid chemistry to water filtration and sewage disposal, nearly all of these have been isolated reports of progress not easy to present as a connected story.<sup>1</sup> The work at the Milwaukee Station, on the other hand, has been on a larger scale than anything previously attempted, so far as the writer is aware, and a complicated problem has been brought to a highly successful conclusion by applying the principles of colloidal behavior. In order to serve the purpose of this chapter to the best advantage, it has been decided to utilize all of the limited space available for as detailed an account as possible of the work done at Milwaukee, especially since it has a fundamental bearing upon methods of water filtration and other methods of sewage disposal.<sup>2</sup>

<sup>1</sup> A bibliography containing 606 abstracts of general papers, patents, etc., published prior to the inauguration of the line of investigation described in this chapter, may be found in the book, "The Activated Sludge Process of Sewage Treatment," by J. Edward Porter, published in Jan., 1921, by the General Filtration Co., Inc., Rochester, N. Y..

<sup>2</sup> Some phases of this work are described in greater detail in articles by Wilson, Copeland and Heisig. See *J. Ind. Eng. Chem.*, **13** (1921), 406; **14** (1922), 128; **15** (1923), 956; *J. Soc. Leather Trades Chem.*, **5** (1921), 268; *J. Am. Water Works Assoc.*, **8** (1921), 486; Annual Reports of Milwaukee Sewerage Commission.

## PURIFICATION OF SEWAGE

When air is bubbled through neutral sanitary sewage at a temperature of about  $20^{\circ}\text{C}$ ., the bacteria and colloiddally dispersed materials tend to agglomerate into masses capable of settling out when the supply of air is cut off, leaving a clear, supernatant liquor. If the clear liquor is decanted off and the residual sludge

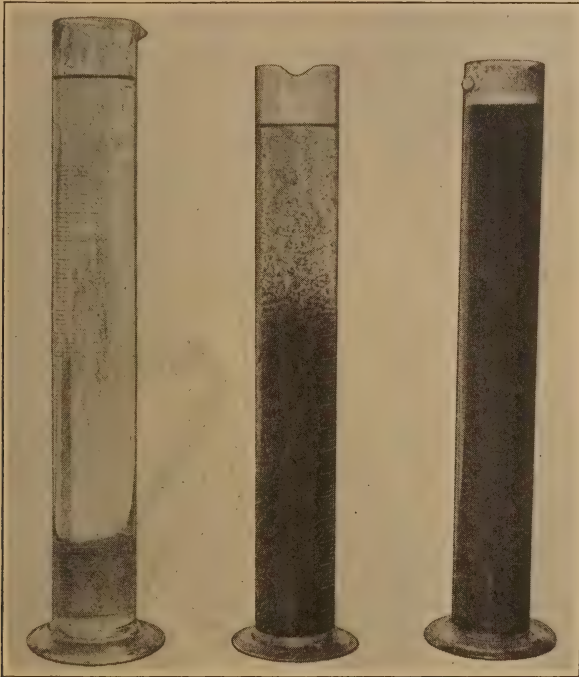


FIG. 1.—At right—raw sewage; middle—sludge beginning to settle; at left—effluent decanted from sludge.

transferred quickly to a fresh supply of raw sewage, clarification of the sewage, upon aeration, occurs at a much greater rate than in the absence of added sludge. Sludge accumulated in this way is known as *activated* sludge. It effects the purification of sewage, apparently, by occluding the bacteria and colloiddally dispersed materials. (Fig. 1 shows the appearance of raw sewage, partially settled sewage, and the decanted effluent.)

In practice, the raw sewage is first passed through bar screens to remove the large materials, then through grit chambers, where the heavy materials settle out, and then through fine, revolving drum screens. It then enters a series of aeration tanks along with activated sludge from the thickeners. The raw sewage contains about 250 parts per million of suspended and colloiddally dispersed matter and activated sludge is added so as to increase this value 10 times. The aeration tanks are 15 ft. deep and have bottoms fitted with filtros plates, through which air is forced. The average time of passage of the sewage through these tanks is about 6 hours, during which time about 1,500 cu. ft. of air have passed through each thousand gallons of sewage. The sewage then passes into a Dorr thickener, where the clarified liquor is decanted over a weir and the sludge, concentrated to about 2 per cent of solid matter, is drawn off from the bottom, part being returned to the raw sewage line and the rest being sent to be dewatered and dried, so as to make its shipment as fertilizer practicable.

The activated sludge removes from the sewage from 95 to 99 per cent of both the bacteria and the suspended and colloiddally dispersed materials. The effluent from the Dorr thickeners, which is relatively pure, is allowed to flow directly into Lake Michigan. It was the necessity for running the sewage effluent directly into the source of the city's supply of drinking water that made it imperative to adopt the activated sludge process, since this process furnishes a purer effluent than any other known.

A demonstration plant capable of handling about 200,000 gal. of sewage daily was erected, so that a study might be made of the process in great detail. It was found that a satisfactory degree of purification of the sewage could be obtained at all times of the year, but a very serious weakness in the process was discovered when it was found that the waste sludge could not be dewatered satisfactorily, by ordinary filter pressing, during the period from November to July.

#### DEWATERING WASTE SLUDGE

The temperature of the raw sewage was found to vary from about 7°C. in winter to about 22°C. in summer. In September, after the process has been operating at maximum temperature



for some time, the sludge is of such character that it settles rapidly in the Dorr thickeners and can be further freed from about 90 per cent of its remaining water very easily by ordinary filter-pressing. In February, however, the sludge assumes a very different character; it does not settle rapidly, but tends to become dispersed easily, and attempts to filter-press it without special treatment resulted only in dismal failure. It was apparent that the success of the entire project depended upon finding some practical means for dewatering the waste sludge at all times of the year. The plant was designed to handle 85,000,000 gal. of sewage per day, yielding 1,275,000 gal. of sludge containing 2 per cent of solid matter to be concentrated, by filter-pressing, to a cake containing over 20 per cent of solid matter. Since it appeared that the solution of the problem lay in the realm of colloid chemistry, the Sewerage Commission, in October, 1920, called in the writer to direct a series of investigations in the hope of finding a practical solution of the problem. It is with this practical solution that this chapter deals.<sup>3</sup>

### DEGREE OF DISPERSION

The entire problem of the activated sludge process appears to be one of regulating the degree of dispersion of the solid matter derived from the sewage and the degree of swelling of the jelly constituents. In the aeration tanks, purification of the sewage is effected by the highly dispersed material joining the coarse, activated sludge, which settles quickly upon standing, thus permitting the clarified solution to be decanted off into the lake. The further removal of water from the settled sludge also depends upon the degree of dispersion. The aggregates formed in the aeration tanks may be coarse enough to settle sufficiently rapidly to permit the continuous purification of sewage, but yet too fine to permit of dewatering by ordinary filter-

<sup>3</sup> Acknowledgment is made of the invaluable assistance rendered by members of the organization and others, especially Commissioner Victor H. Kadish, who first suggested that the writer undertake this work, Chief Engineer T. Chalkley Hatton, who helped to guide the work into practical channels, Henry Mills Heisig, who directed the laboratory work, William R. Copeland, who directed the plant work, and George S. Backus, who first applied heat to the sludge for dewatering by means of the Oliver filter.

pressing, the finely divided matters quickly clogging, or blinding, the filter cloth. During the winter months it was found that the sludge formed in the aeration tanks was always coarse enough to permit satisfactory purification, but not coarse enough to be filter-pressed efficiently.

Part of the sludge consists of organized jellies, such as fibrous protein matter. The degree to which the sludge can be freed from water by filter-pressing depends not only upon the fineness of subdivision of a portion of the sludge, but also upon the extent to which the jelly constituents are swollen with water. A mass of fibrous protein matter may hold water in two very different ways: in the interstices between the fibers, and from which it may be forced out by the application of relatively slight pressure and, secondly, in the substance of the fibers, like the water absorbed by a solid block of gelatin, and from which the water cannot be removed mechanically, except by the application of enormous pressure. The sludge will be in its best condition for filter-pressing when the individual particles are as coarse as possible and the swelling of the jellies is at a minimum value. Fortunately, the tendency for the particles of a protein dispersion to unite to form large aggregates is greatest at the isoelectric point of the protein, which coincides also with its point of minimum swelling. Loeb<sup>4</sup> has shown this repeatedly with gelatin dispersions.

#### RELATIVE FILTERING EFFICIENCY AS THE STANDARD UNIT OF MEASUREMENT

Since the practical problem to be solved was the preparation of the sludge in condition suitable for filter-pressing, it seemed logical to use as a measurement of this condition the rate of filtration of the sludge under standard conditions. The apparatus used to make this measurement, and also to study the effect of a change in any variable factor, consists of a battery of uniform Büchner funnels set in filter flasks, all connected to one pump furnishing a high vacuum. As a standard, a sample of sludge was selected of such condition that its rate of filter-pressing was considered on the border line between satisfactory and unsatis-

<sup>4</sup>LOEB, JACQUES: "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Book Co., New York.

factory. It was found that 500 cc. of such sludge diluted to contain 1 per cent of solid matter could be dewatered on a standard laboratory filter in just 20 minutes. This made it convenient to define the *relative filtering efficiency* of any sample of sludge as 2,000 divided by the number of minutes required to filter 500 cc. of 1 per cent sludge through a standard filter. This gives the sludge which was only just satisfactory a relative filtering efficiency of 100. This number is, of course, purely arbitrary, but it will do as well as any other, since it is only the comparison of rates of filtration that count. Changing the size of the Büchner funnels or the kind of filter paper employed merely changes the constant in the equation of proportionality between the laboratory measurements and the large-scale plant operation. Two years of operation of large-scale filter-pressings show that the efficiency obtained for any given type of sludge is directly proportional to the value defined as relative filtering efficiency, provided the filter press is operated under fixed conditions, including the delivery of the same amount of sludge per unit area of filter cloth in each pressing.

Having adopted a standard method of measurement, the next step was to study the effect of the several important variable factors upon the condition of the sludge. Studies were made of the variable factors operating in the aeration tanks as well as those involved in the direct treatment of the sludge for filter-pressing. The figure for relative filtering efficiency was found to be very sensitive to the variable factors operating in the aeration tanks and showed a wide daily fluctuation. There was a well-defined average trend shown throughout the year, however, from the very low value of 5 in February to 100 in September, falling again to 5 the following winter. Only in the late summer was it possible to filter-press the sludge satisfactorily without special treatment.

#### EFFECT OF pH VALUE

It is now well known that colloidal behavior is markedly affected by change of pH value. That pH value would prove to be an important variable factor in this work was doubly apparent because it had already been found that the addition of a small amount of sulfuric acid to the sludge greatly facilitated filter-

pressing in most cases. The effect of pH value was determined by adding variable amounts of standard solutions of sulfuric acid or sodium hydroxide to the samples of sludge when diluting to the standard content of solid matter, so as to give a wide range of pH values. All samples were thrown onto filters at the same time and the relative filtering efficiencies noted.

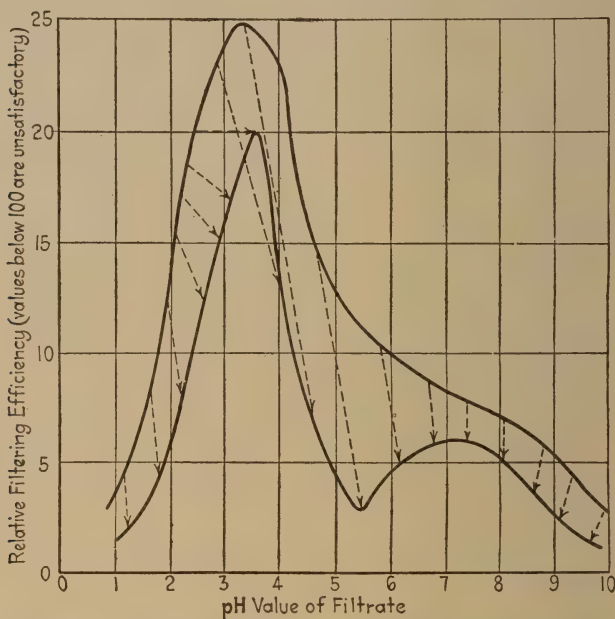


FIG. 2.—Effect of change of pH value upon the relative filtering efficiency of winter sludge. The upper curve represents series filtered 15 minutes after acidifying; the lower curve a series filtered 24 hours after acidifying; dotted lines connect points representing samples of sludge receiving identical treatment.

Figure 2 shows the results obtained for a typical, septic sludge of February, the upper curve representing a series filtered 15 minutes after treating with acid or alkali and diluting and the lower curve an identical series filtered 24 hours after treating. The sludge before treating had a pH value of 7.8; lower values indicate treatment with sulfuric acid and higher values treatment with sodium hydroxide. Dotted lines connect points in the two curves representing samples receiving identical treatment.



The upper curve shows a clearly defined point of maximum at pH 3.4. Curves of this type have been obtained for representative samples of sludge daily for over two years and it is remarkable that the optimum value always occurs at pH 3.4, regardless of the condition of the sludge or of great changes occurring in the proportions of different industrial wastes entering the sewers from time to time. By adding enough sulfuric acid to lower the pH value from 7.8 to 3.4, we have brought about an increase in relative filtering efficiency from 5 to 25, a large amount, but still insufficient to permit of satisfactory filtering.

The lower curve shows the marked changes undergone by the septic sludge in standing for 24 hours at different pH values. At all pH values the sludge showed a tendency to become redispersed, but this was most pronounced at a pH value of about 5.5. This led us into a line of investigation, too extensive to describe in detail here, the results of which indicated that septic action in activated sludge proceeds at the greatest rate at a pH value of 5.5 and that dispersions of sludge have two points of optimum precipitation, at pH 7.4 and 3.4.

#### AERATION VERSUS PUTREFACTION<sub>7.4</sub>

In order to make laboratory studies of the effect of pH value and other variable factors upon the aeration process, a battery of stoneware cylinders was used. In the bottom of each was placed a filtros plate, having an area of 1 sq. ft., through which air, or other gas, could be forced. The cylinders were surrounded by water jackets for regulating the temperature. Each was 15 in. in diameter and had a capacity of about 70 gal. Air was forced through the filtros plates at the rate of 0.45 cu. ft. per minute. After aerating sludge in these tanks under fixed conditions, it was allowed to settle and the clear solution decanted off.

When winter sludge was diluted and aerated in one of these tanks at a pH value of 7.4 and a temperature of 20°C., its condition gradually changed from that of winter sludge to that of summer sludge. When sludge so treated was allowed to stand long enough to become septic, its condition gradually reverted to that of winter sludge. This action was found to be practically completely reversible. The average size of the sludge particles was increased by aeration and decreased by septic action.

In studying the effect of pH value upon the aeration process, it was found difficult to maintain pH values quite constant in each tank, but the results showed unmistakably two points of optimum, at pH 3.4 and 7.4 and a point of minimum efficiency at 5.5. The curves obtained were of the same type as the lower curve of Fig. 1. At pH 3.4, aeration increased the relative filtering efficiency at the greatest rate. At pH 5.5, the relative filtering efficiency decreased continually, in spite of the aeration, while at 7.4 it increased markedly, although not so rapidly as at 3.4.

When operating at a pH value of 7.4, it was found necessary to have oxygen present in the gas used for aerating, in order to bring about an increase in relative filtering efficiency; pure hydrogen gas gave only a decrease. At pH 3.4, oxygen was found to be necessary when the sludge was septic, but apparently not when in initially good condition; even hydrogen gave an increase in relative filtering efficiency. The oxygen appeared to be beneficial in checking the disintegrating action of putrefactive bacteria sufficiently to permit the building up of large aggregates under conditions favoring precipitation of the sludge. The addition of xylene to the aeration tanks caused a decrease in relative filtering efficiency, regardless of the gas used in aerating the sludge. The xylene appeared to coat the sludge particles in such manner as to prevent coalescence.

#### EFFECT OF ALUMINUM SULFATE

The well-known power of polyvalent ions to cause precipitation of colloiddally dispersed materials carrying an electrical charge of opposite sign led us to study the effect of salts with polyvalent ions. Since the sludge apparently always carries a negative charge at pH values higher than 3.4, the choice seemed to lie among the polyvalent metal ions, such as aluminum, ferric, and chromic ions.

The effect of adding aluminum sulfate to February sludge is shown in curve *B* of Fig. 3. For each gram of dry solid matter in the sludge, there was added 0.1 g. of commercial aluminum sulfate, in diluting to standard condition. In this series only the pH value was varied, by the addition of sulfuric acid. It will be noted that a point of optimum is obtained at pH 4.4.

This may be explained by assuming that at this point the positive charge on the aluminum ions just balances the negative charge on the sludge. At pH values below 3.4, where both sludge and aluminum are positively charged, the aluminum apparently adds

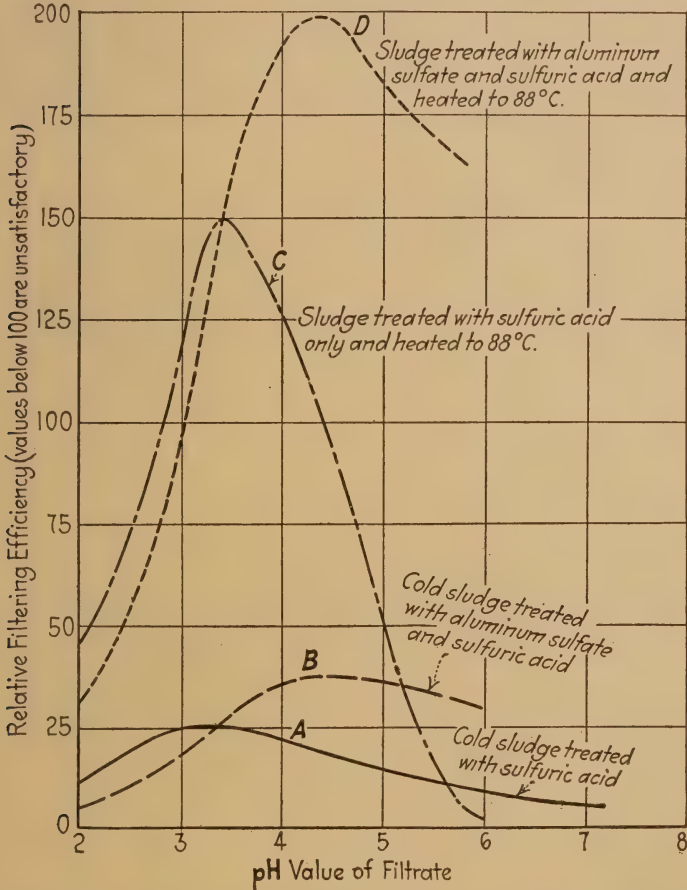


FIG. 3.—Effect of change of pH value upon the relative filtering efficiency of winter sludge treated in different ways.

its charge to that of the sludge and the relative filtering efficiency is decreased. The increase in efficiency obtained by the use of both aluminum sulfate and sulfuric acid is about 50 per cent greater than with sulfuric acid alone, but it is still insufficient

to enable one to filter February sludge efficiently. Somewhat greater increases in efficiency are possible, using larger amounts of aluminum sulfate, but the cost hardly warrants the use of larger quantities.

Chromic salts gave results almost identical with those obtained with aluminum sulfate. A difficulty is encountered in the use of ferric salts in their tendency to become reduced to the ferrous state. Ferrous salts proved to be practically no more effective than sulfuric acid alone, which is not surprising in view of the divalence of the ferrous ion.

#### EFFECT OF TEMPERATURE

Temperature is another important factor in the precipitation of sols. Figure 4 shows the effect of increase of temperature upon the relative filtering efficiency of February sludge with and without the addition of aluminum sulfate and with the pH value adjusted to the optimum value in each case. Where sulfuric acid alone is used, an optimum value is obtained at a temperature of about 88°C., above which a portion of the sludge seems to disintegrate. With aluminum sulfate equal in quantity to 0.1 of the weight of dry solid matter in the sludge, and sulfuric acid to make pH 4.4, we get a curve increasing in value at all points up to the boiling point of water.

Curves *C* and *D* of Fig. 3 show the effect of pH value upon heated sludge. Curve *C* shows the effect upon sludge treated with sulfuric acid only before heating and curve *D* the effect upon sludge treated with aluminum sulfate and sulfuric acid before heating. By acidifying to make pH 3.4 and heating the sludge to 88°C., we get a relative filtering efficiency of 150 against only 5 for untreated sludge. The use of aluminum sulfate, in addition to the acid, enables us to raise this value to 200, by bringing the sludge to a temperature of 100°C. This represents an increase in filtering efficiency of approximately 4,000 per cent and brings winter sludge into a condition such that it filters twice as rapidly as untreated summer sludge.

In order to get a large increase in relative filtering efficiency by the application of heat, it is necessary to adjust the pH to the proper value. As will be noticed in Fig. 3, heating sludge having a pH value greater than 5.6 causes a marked decrease



in filtering efficiency. When applying heat to the sludge, we get a point of optimum at pH 3.4, but not at 7.4, as in ordinary aeration.

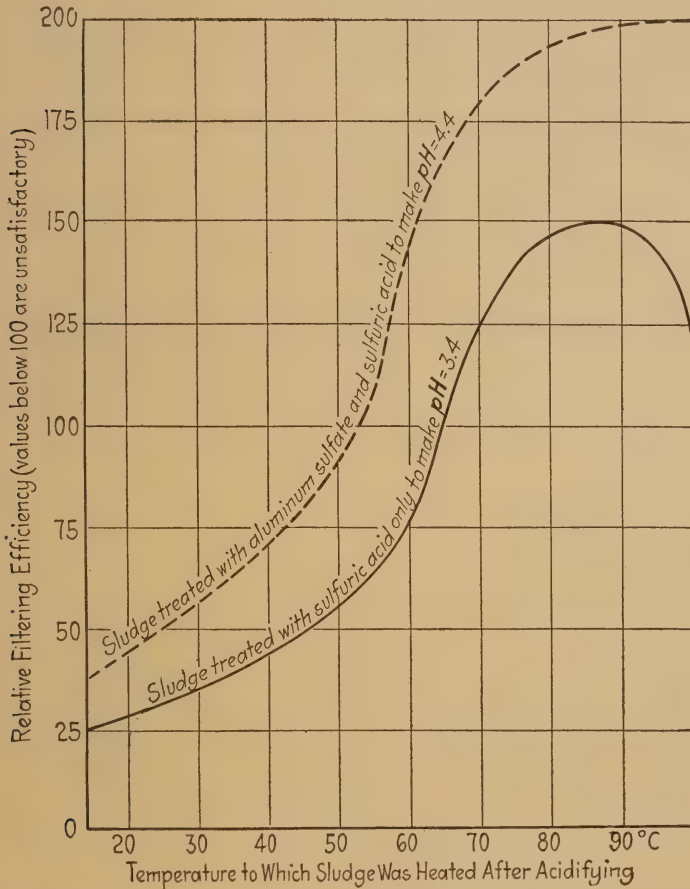


FIG. 4.—Effect of change of temperature upon the relative filtering efficiency of winter sludge previously treated with aluminum sulfate and sulfuric acid or with sulfuric acid alone.

Although it seemed probable that the difference between summer and winter sludge was due to differences in temperature of the raw sewage, it was deemed advisable to settle this point definitely, because it has been suggested that the summer con-

dition might be due to certain organisms present in the sewage in large quantities only in the late summer. In order to do this, the experimental plant was divided into two independent systems at the beginning of the year 1922. One of these systems was operated in the normal manner and the other was operated exactly like it, except for the fact that all of the raw sewage entering

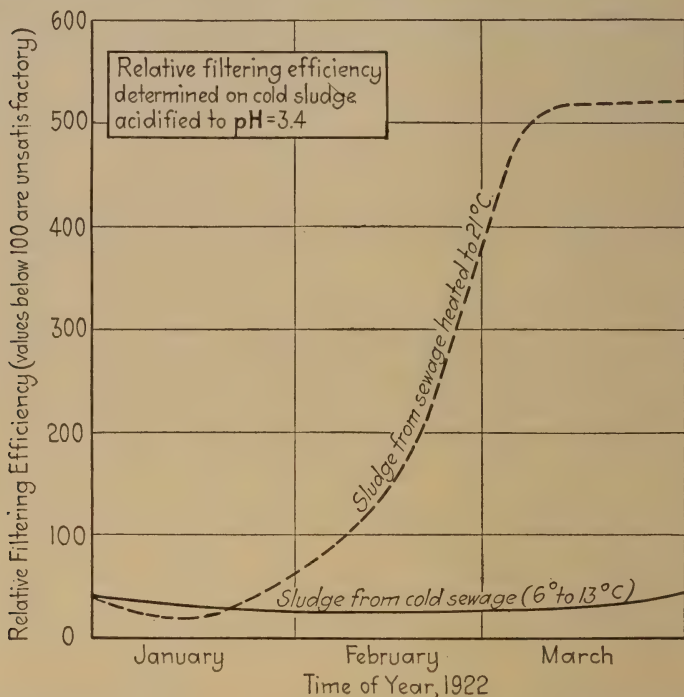


FIG. 5.—Effect of temperature of the raw sewage upon the relative filtering efficiency of the activated sludge produced.

it was heated to a temperature of 21°C. The sludge from the cold system, in which the temperature varied from 6 to 13°C., was characteristic of winter sludge. In the heated system, however, the quality of the sludge at first became worse, but after about two weeks it began to improve, and the average size of the particles to increase, until early in March the sludge was typical of the best ever obtained in September. The curves shown in Fig. 5 represent the relative filtering efficiencies obtained when

the pH value was adjusted to 3.4 with sulfuric acid before filtering.

The experiment shows clearly that it is the higher temperature that is responsible for the building of large particles of sludge from the smaller ones. The decrease in quality of the sludge during the first two weeks of January may be attributed to increased putrefaction in the Dorr thickener, caused by the higher temperature. As the condition of the sludge entering the thickener improved, the tendency towards septic action decreased correspondingly.

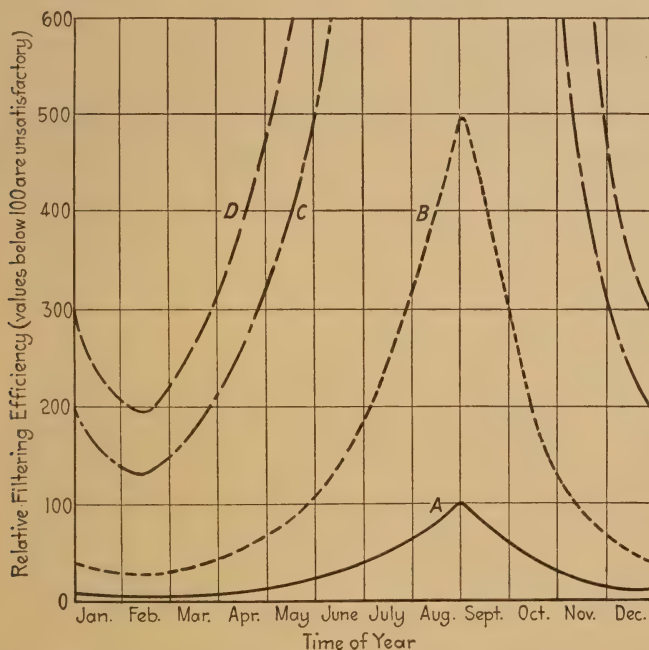


FIG. 6.—Seasonal changes in the relative filtering efficiency of activated sludge treated in various ways. A, Cold sludge not treated. B, Cold sludge treated with sulfuric acid to make pH 3.4. C, Sludge acidified to make pH 3.4 and then heated to 88°C. D, Sludge treated with aluminum sulfate and sulfuric acid to make pH 4.4 and then heated to 88°C.

### SEASONAL CHANGES

Figure 6 illustrates the seasonal changes in the sludge treated in different ways. The curves were plotted from average values obtained during 2½ years of continuous observation and experi-

menting. Actually, each of the curves is subject to a rather wide daily fluctuation, due to variations in temperature, septic action in the Dorr thickeners, and other variable factors, but the general trend is unmistakable and recurs each year. A very curious point to be noted is that any given treatment multiplies the relative filtering efficiency by a constant factor, regardless of the initial condition of the sludge. It should also be noted that the sludge can be dewatered in a highly satisfactory manner at all times of the year, if properly heated and acidified.

### PRACTICAL APPLICATION

In the large-scale experimenting to find a practical means of dewatering winter sludge, many types of apparatus were used, including a centrifuge and several types of pressure filter presses, but the work with these cannot be described for lack of space. In the new plant, the dewatering operation will be performed by 24 Oliver continuous vacuum filters, each 11 ft. 6 in. in diameter and 14 ft. long, with 495 sq. ft. of effective filtering surface. In the experimental plant, we used a small filter of this type, 3 ft. in diameter and 2 ft. long, with a filtering surface of 20 sq. ft. The filter consists of a revolving drum covered around its side with twill cotton filter cloth, set in a tank of sludge so that 40 per cent of the filter cloth is always submerged. Under the filtering surface, the drum is fitted with a piping system arranged to exert either a pressure or vacuum. As the drum revolves, any given point on the filter cloth travels through the sludge liquor 40 per cent of the time of a complete revolution and through the air the remaining 60 per cent. When the cloth is submerged, and during a portion of its journey through the air, a vacuum is applied. When any point in the cloth approaches the take-off, pressure is applied to assist in the removal of the partially dewatered sludge cake. The whole system is continuous, a vacuum being applied at all points except those in the vicinity of the take-off, where pressure is applied.

The sludge delivered to the filter tank was always acidified first and then heated. When the heat was applied before the sludge was properly acidified, much poorer results were obtained, as would be expected from the laboratory experiments described above.



When the laboratory data were first applied to the larger filter, there appeared to be a number of serious discrepancies and the cause had to be found. In one test, a given treatment of the sludge showed an increase of 100 per cent in relative filtering efficiency in the laboratory, but when the same treatment was applied to the sludge entering the filter tank, an increase of

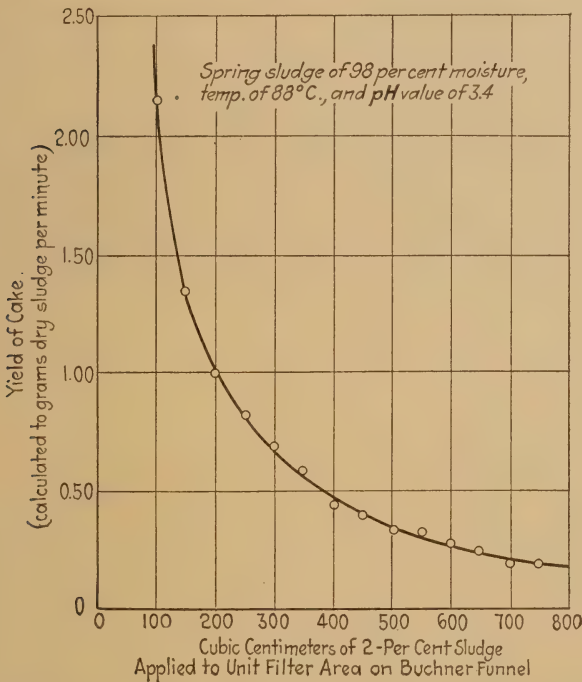


FIG. 7.—Showing how yield per unit of time is affected by the amount of sludge applied to unit filter area.

only 40 per cent was observed. It was noted, however, that the cake was thicker than was the case when the given treatment was omitted. This was clearly the reason for the discrepancy for, as we had previously observed, the relative filtering efficiency decreases with the amount of sludge applied per unit of filter area. How great this decrease is can be seen by reference to Fig. 7. When the speed of the drum in the Oliver filter was increased to the point where it picked up the same quantity of

sludge per square foot of filter cloth in the specially treated sludge as it had in the sludge not so treated, the increase in efficiency was then 100 per cent, exactly as in the laboratory tests.

Figure 8 shows how the yield of cake delivered by the Oliver filter varies with the speed of the filter drum. With increasing

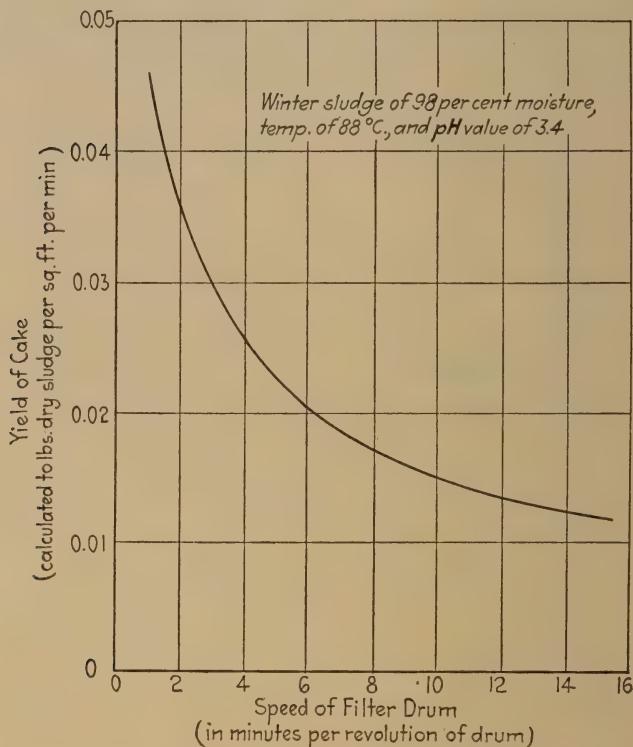


FIG. 8.—Showing how the efficiency of the Oliver filter is decreased by lowering the speed of the filter drum.

speed, there is an increasing yield, but a thinner cake, which increases the difficulties at the take-off. The most efficient speed is that which gives a cake so thin that it can just be handled properly at the take-off.

Another troublesome variable proved to be the blinding of the filter cloth. In the laboratory, fresh filter papers are used for

each test, but on the big filter the same cloth is used for many tests. It frequently becomes blind and must be washed thoroughly before filtering can be continued. This variable degree of blindness has been the cause of a number of apparent discrepancies between laboratory and plant data.

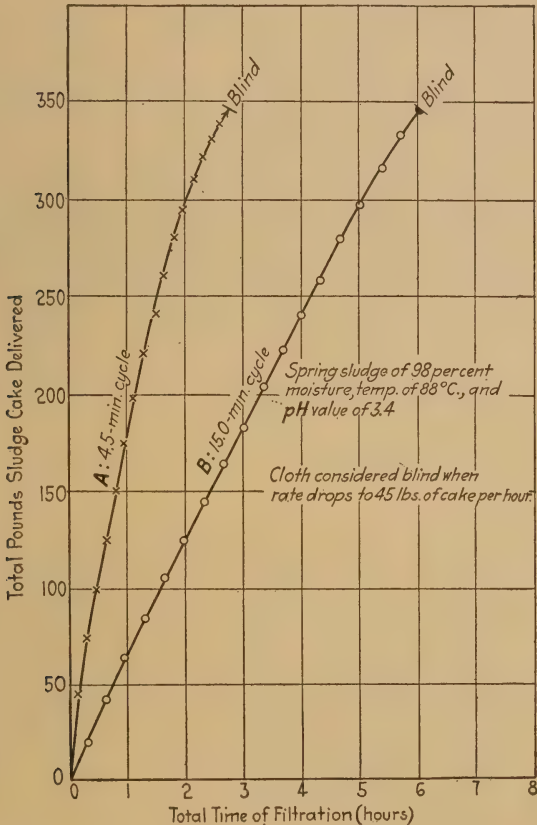


FIG. 9.—Showing how the yield of cake varies with the time of filtration until the filter cloth becomes blind. A, using a drum speed of 4.5 minutes per revolution. B, using a drum speed of 15.0 minutes per revolution.

It was found, however, that the blinding of the filter cloth follows a definite rule. Figure 9 shows the results of two runs made on the same sludge. In one case the drum was made to revolve once in 4.5 minutes; in the other, once in 15 minutes.

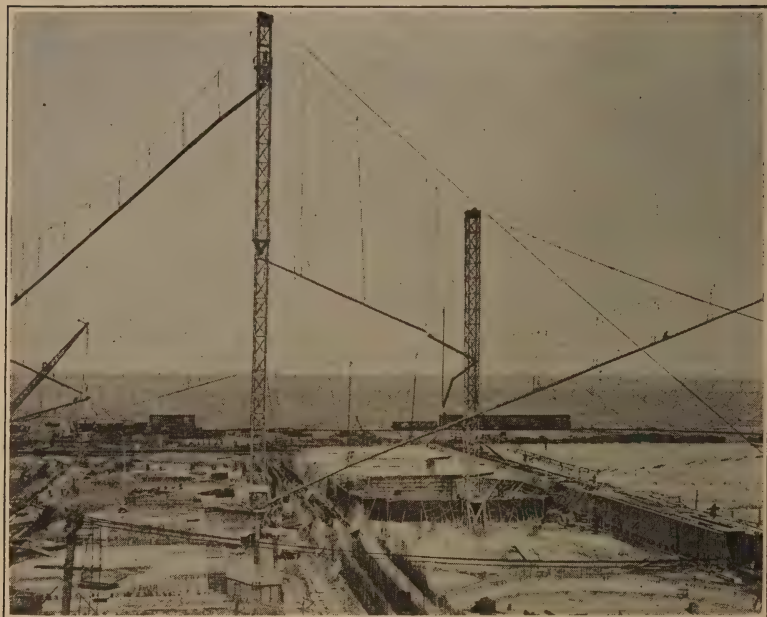


FIG. 10.—Milwaukee Sewage Disposal Plant, August, 1923. Settling tanks in foreground; aeration tanks to extreme right and left—all in various stages of construction.



FIG. 11.—Milwaukee Sewage Disposal Plant, August, 1923. A battery of aeration tanks under construction.





FIG. 12.—Milwaukee Sewage Disposal Plant, August, 1923. Looking into one of the grit chambers through which the sewage flows before entering the fine screens, prior to aerating.

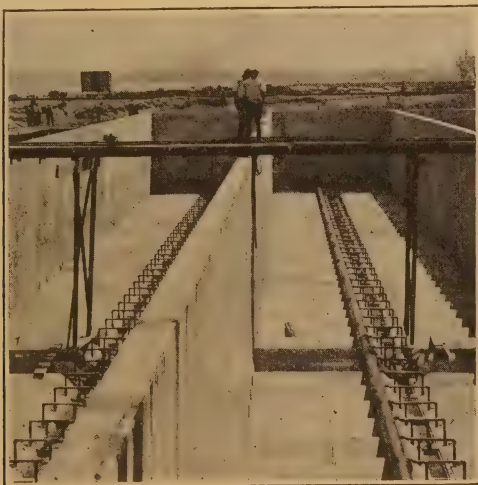


FIG. 13.—Milwaukee Sewage Disposal Plant, August, 1923. Looking into one of the aeration tanks.

The cake was weighed at intervals and the total yield plotted against the running time. In each case the cloth was thoroughly washed before the run was started and the drum was stopped as soon as the rate of delivery of cake fell to 45 lb. per hour, which was taken as the blinding point. It will be noted that blinding is a direct function of the quantity of sludge filtered and is independent of the time required for the operation. By tripling the drum speed, the quantity of sludge picked up per revolution was reduced to two-thirds, but the greater speed gave a net increase of about 100 per cent in yield per unit of time. The amount of sludge which the filter can deliver before becoming blind varies with the condition of the sludge, being greatest in September and least in February. It is also clear that the drum speed should be varied with the condition of the sludge in order to get the highest efficiency at all times, since, when run at constant speed, the filter picks up a thicker cake the better the condition of the sludge.

With the factors of drum speed and blinding under control, there appeared to be no difficulty in duplicating laboratory results in the plant.

A number of photographs showing the Milwaukee Sewage Disposal Plant in various stages of construction are reproduced in Figs. 10 to 13.

#### THEORETICAL

The behavior of the sludge at a pH value of 3.4 seems to the writer to indicate that here we are dealing with a mechanism similar to the aggregation of gelatin molecules and particles at the isoelectric point, or to the precipitation of sols. This mechanism is probably the same both in the aeration tank and in the treatment of the settled sludge.

At a pH value of about 7.4, however, the building up of large particles in the aeration tank may be governed by other forces. In dewatering sludge in good condition, we find a point of optimum only at 3.4 and not at 7.4. When sludge at pH 7.4 is heated to 80°C., its condition actually becomes much worse, just the reverse of what happens at 3.4. In aerating at pH 7.4, oxygen appears to be essential to the action; in fact, aerating without oxygen is harmful.

It appears to the writer possible that a relation exists between the action occurring in the aeration tanks at pH 7.4 and the building of tissues in the animal body. In a lecture Dr. Bradley<sup>5</sup> pointed out that the stability of the body tissues is decreased when the oxygen supply is cut off, and the pH value, by the introduction of acid, is brought below 7.4, the normal value for the blood in living tissues. Immediately after the death of an animal, there is a fall in the pH value of the blood from 7.4 to values below 7.0 and the tissues begin to atrophy. This action can be accelerated by the addition of acid, although a great excess of acid retards the action.

When the air supply is cut off from the aeration tanks, the large particles of sludge immediately begin to break down. As in the case of animal tissues, we found that adding just enough acid to bring the pH value to 6.0 caused the sludge particles to atrophy with extreme rapidity, while this action was retarded by adding enough acid to lower the pH value to the vicinity of 3.4. But when the pH value of the atrophied sludge is again brought to 7.4 and it is aerated, the large particles are gradually rebuilt. If we may liken the action in the aeration tanks to the building of tissues in the animal body, it will help to explain the remarkable constancy of properties of activated sludge in the face of marked changes in composition of the raw sewage.

#### SUMMARY

By applying what has been learned of the effect of pH value, temperature, and polyvalent ions upon colloidal behavior in general to the problem of dewatering activated sludge, it has been shown how to increase the efficiency of this operation by about 4,000 per cent, thus removing the one weak point in what was otherwise the most efficient process known for purifying sewage.

<sup>5</sup> BRADLEY, H. C.: "The Chemical Mechanism of Atrophy in the Animal Body," Lecture delivered before the Milwaukee Section of the American Chemical Society, Mar. 23, 1923.





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